THE UNIVERSITY *of* EDINBURGH

PHOSPHATE AND AMMONIUM REMOVAL FROM WASTE WATER, USING CONSTRUCTED WETLAND SYSTEMS

ALEKSANDRA DRIZO

Thesis submitted for the Degree of Doctor of Philosophy in the Faculty of Science and Engineering, Institute of Ecology and Resource Management

UNIVERSITY OF EDINBURGH

1998

DECLARATION

I, Aleksandra Drizo, hereby declare that this thesis was composed by myself, and that the work described was carried out by myself, except for the instance detailed in the acknowledgements. The work presented here has not been submitted in any previous application for a degree.

Aleksandra Drizo

In the temple of science are many mansions... and various indeed are they that dwell therein and the motives that have led them there.

Albert Einstein

THE UNIVERSITY OF EDINBURGH

ABSTRACT OF THESIS

(Regulation 3.5.13)

Name of Candidate Aleksandra DRIZO

Address

Degree PhD *Date* 05.03.1998

Title of Thesis Phosphate and ammonium removal from waste water, using constructed wetland systems

No. of words in the main text of Thesis 38 000

Phosphorus and nitrogen in waste water from sewerage systems contribute to excessive nutrient enrichment of surface waters, presenting a threat to nature conservation, domestic and industrial water supplies, and recreation. The general objective of this research was to investigate phosphate and ammonium removal from waste water by constructed wetland systems (CWS), which are increasingly being used for low-cost water treatment.

Phosphate (P) adsorption capacity and other properties of potential CWS substrate materials (bauxite, shale, burnt oil shale, limestone, zeolite, light expanded clay aggregates (LECA) and fly ash) were investigated. Fly ash and shale had the highest P adsorption values, which were significantly correlated with porosity and hydraulic conductivity. Longer - term experiments with shale and bauxite gave maximum P uptake values of 730 and 355 mg P kg^{-1}, respectively. *Phragmites australis* (common reed) seedlings grew satisfactorily in shale, bauxite, LECA and fly ash. Shale was selected as the most suitable substrate, and used in a pilot-scale CWS in plastic tanks in a greenhouse, with and without *P. australis*, at two input nutrient concentrations and a loading rate of 0.02 m^3 m^{-2} d^{-1}. Both planted and unplanted systems removed 98 - 100 % of P from a synthetic sewage over 11 months. Removal of ammonium N was also complete in the planted tanks, but only 40 - 75 % was removed in the unplanted ones. Corresponding nitrate N removal was 85 - 95% and 45 - 75%. The systems performed as well at high as at low concentration for both phosphate and ammonium. The variations in P and N removal could not be attributed to differences in pH, E_h and temperature, which did not differ significantly between planted and unplanted tanks.

During the experiment, P and N concentrations were determined at 3 depths and 4 positions along the length of the tanks. $H_2PO_4^-$ - P and NH_4^+ - N concentrations were low (< 1.0 g m^{-3}) at all locations in the planted systems, whereas the P concentrations were sometimes twice as high in the unplanted ones. NH_4^+-N in the unplanted systems was relatively high (10 - 30 g m^{-3}) throughout the experiment. NO_3^--N concentrations were very low by comparison. P. precipitation on shale and *P. australis* root and rhizome surfaces was examined by X-ray fluorescence analysis, and by chemical extraction with ammonium acetate, 0.1 M HCl and 2% citric acid. This showed that P, Fe and Al had precipitated on all these surfaces. However, it was not possible to quantify the surface deposits, and further research is necessary.

The hydraulic residence time, flow characteristics and permeability of the shale was investigated by a bromide tracer. The tracer breakthrough curves showed a similar pattern in all tanks, with *ca* 66% of the flow occurring through the bottom zone. However, the actual hydraulic residence time (6 days) was slightly higher than the theoretical one Although there was a significant difference ($p < 0.02$) between the distribution of flow in planted and unplanted tanks, there was no reduction in the reactive pore volume observed in any of the tanks. This confirmed that shale has good permeability properties.

Monitoring of the full-scale systems was carried out during June - September 1995. Although P removal in a planted bed was between 50-75%, the overall performance of the full-scale systems was disappointing, especially for ammonium removal. This was attributed to high loading rates, visibly non-uniform flow and clogged gabions. A bromide tracer study carried out on these systems confirmed the short hydraulic retention times and heterogeneous flow mechanisms in both the unplanted and planted systems.

Results obtained from the pilot scale study do not necessarily provide a quantitative prediction of the performance of larger-scale systems. However, the potential value of a shale-based system has been demonstrated, and this opens a new direction in the design of CWS; most systems built to date in the UK use gravel as a substrate. Shale has proved to have superior properties for P removal and is cheap and readily available in Scotland. Its application as a substrate in a full-scale system remains a subject for further investigation.

Dedication

This thesis is dedicated to my beloved parents Aleksandar and Zorce Drizo. Without their permanent love, support and believing in me this work would have not been possible.

Don't Quit

When things go wrong as they sometimes will
When the road you're trudging seems all up hill,
When the funds are low and the debts are high
And you want to smile, but you have to sigh,
When care is pressing you down a bit,
Rest, if you must, but don't you quit.
Life is queer with its twists and turns,
As everyone of us sometimes learns,
And many a failure turns about
When he might have won had he stuck out;
Don't give up though the pace seems slow-
You may succeed with another blow.
Success is failure turned inside out-
The silver tint of the clouds of doubt
And you never can tell how close you are
It may be near when it seems so far;
So stick to the fight when you are hardest hit
It's when things seems worst
that you must not quit....

Acknowledgements

First of all I wish to acknowledge financial support from CVCP Overseas Research Scholarship Fund (ORS), the Environmental Research Support Scheme (ERSS) of the Soros Foundation (Central European University, Budapest) and the Scottish Office Agriculture and Fisheries Department (SOAFD). I also wish to thank my father, Mr Aleksandar Drizo, as without his love, understanding and financial support this work would have not been possible to complete - despite the aforementioned scholarships.

I am indebted to my supervisor, Professor John Grace for bringing me to the University of Edinburgh. Not only has he taught me a great deal, but he has always been enormously supportive throughout my work on the thesis. I would also like to thank him for being a true friend.

Many thanks to my other two supervisors, Professor Keith Smith and Mr Alan Frost for their advices throughout the thesis.

The work in this thesis has benefited greatly from discussions with Professor Hans Brix of Århus University, Denmark and Mr Ron Speirs of Scottish Agricultural College at the outset of the research and Dr Peter Hiley of Yorkshire Water, England - throughout the dissertation.

The laboratory of the Scottish Agricultural College (SAC) has provided a very stimulating environment for research. Here I would in particular like to thank Mr Rab Howard, Mrs Frances Wright and Ms Lesley Swan for being always ready to help. I am also extremelly grateful to Billy, Alisdair, June, Willie and Graham for letting me use their equipment at Chemical Analytical Laboratory (CAL). Many thanks to Irene, Daina and Lillias as well as Ina, Tricia and Nancy for listening to me and being my friends.

I am indebted to Mr Jack MacGowan and John Swanly of SAC for providing the

equipment for P analyses - without their help and support the carrying out of laboratory analyses would not have been possible.

Many thanks to:

Mr J. Pearson of Wemyss Brick Co., Fife, Scotland for the supply of shale material and Mr T. Cole of Alcan Chemicals, Europe, Burntisland, Fife, Scotland for the supply of bauxite; Mr Jim Taylor of Fife Regional Council for providing me with the information on the Valleyfield reed bed system; Dr G. Angel and Mrs D. James, Department of Geology, University of Edinburgh, for help with XRF analyses; Mr John Findlay of the Scanning Electron Microscopy Unit, University of Edinburgh and Dr Gordon Lindsay of Napier University for their help with SEM and EDAX analyses; Mr Paul Johnstone for his help in the establishment of the greenhouse systems and his help with the field work. It has been a great pleasure and fun working with him.

It has been my pleasure to discuss many subjects with many people. I would like to mention, in particular, Professor Peter Jenssen of Agricultural University of Norway, Ås, Norway; Professor George Tchobalogonous of the University of Davis, California; Dr Anders Finsson of Stockholm Water Company, Stockholm, Sweeden; Mr Johanness Laber, of Universität für Bodenkültur Wien, Austria; Ms Lena Johansson of Royal Institute of Technology, Stockholm, Sweeden; Ms Tong Zhu of Agricultural University of Norway, Ås, Norway; Mr Geir Norden of Norsk Leca, Oslo, Norway; Dr Aris Gerakis, of Michigan State University, USA. They have all remained rich sources of ideas and individual stimulation.

I would also like to thank to my colleagues from the SAC - Dr Simona Castaldi, Dr Andy Vinten, Dr Paul van Gardingen, Mr Eric Hayward, Dr Ian McTaggart, Dr Piedad Martin Olmedo. Many thanks to my office mates Simo, Karen and Franz for tolerating the many moods of writing up.

Above all many thanks to Francis Daunt for being always by my side not just in my work, but more importantly, in my heart. I would also like to thank Francis for his

help, support, understanding and enormous patience throughout the whole period of the thesis. In particular for his help in getting the materials from Fife, establishment of the greenhouse tanks and in carrying out bromide tracer studies. Many thanks to Simic for being such a wonderful and supportive friend, flatmate and officemate, for being able to tolerate my 'impossible' nature and for always being able to bring smile to my face. Thanks to Pietro for his great sense of humour. I would also like to thank the former student of mine, Hannot Elorriaga - it was a great pleasure working with him. Many thanks to Alex for his love, support, and understanding every since we met in 1995. In particular, for his help with carrying out bromide sampling in spring of 1996 and for being with me at the most difficult period of my traumatic illness. I am endlessly grateful to my sister Maja for her love and support and for being always there for me. Many thanks to Zile for getting in touch and being with me during my ilness for the second time.

Many thanks to a number of friends who kept me alive via e-mail. In a first place Francis Daunt and Alex Simpson. I would like to thank Aris - we had many fruitful discussions; Many thanks to Kurt - for being always so supportive and a very special friend. Here I would like to thank again Simo - for surviving reading through long e-mails; Dr Peter Hiley, Dr Anders Finsson, Mathew Wilkinson and lately, Professor Yves Comeau and Professor Gideon Oron.

Finally, I would like to thank my new friends Mateja, Mike, Daniel, Martin, Boaz and Aspa for being there when I needed them the most. In particular, I am grateful to Mikkel, for not only that he has been there during the final stage of my writing up - but for being my inspiration and making the whole process a much nicer experience for me.

Above all, I am grateful to my parents for being so wonderful, for their endless love, support and trust in me during the past 4½ years. *Beskrajno HVALA na ljubavi, paznji i paricima najbolji, nasladji i najmiliji makic i tatkice na celome svetu.*

Chapter 1: Introduction and literature review

Chapter 4: Phosphate and ammonium distribution in a greenhouse constructed wetlands

Chapter 5: Investigation of hydraulics and flow regime in constructed wetlands with horizontal subsurface flow, using bromide tracer

Chapter 8: Discussion and conclusions

List of Figures

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 5

Chapter 6

Chapter 7

List of Plates

Chapter 3

Chapter 6

Appendix 2

Appendix 3

List of Tables

Chapter 1

Chapter 2

Chapter 3

Chapter 4

Chapter 6

Chapter 7

Chapter 1: Introduction and literature review

1.1 Background

Prior to 1800, the deterioration of water quality caused by pollution was not a general problem because human populations were small and most people lived in scattered rural communities. Therefore, the natural self-purification properties of rivers could cope with the wastes dumped into them (Mason, 1991).

Water pollution became a severe problem with industrialization, coupled with the rapid acceleration in population growth. As a result, domestic, industrial and agricultural users produced large quantities of waste products, and waterways provided a cheap and effective way of disposing of many of these. This led to *eutrophication*, which can be defined as the enrichment of waters by nutrients, mainly phosphorus and nitrogen (Harper, 1995). Of the two, phosphorus is more often rate-limiting for algal growth in fresh water, and an influx from anthropogenic sources, e.g. waste water, can create such problems as algal 'blooms', resulting in a deterioration of water quality and the depletion of dissolved oxygen, which in some cases can cause the death of fish (Yeoman *et al.*, 1988; Horan, 1990).

As a result of these environmental problems, nutrient removal from wastewater, in order to reduce eutrophication in inland waters, estuaries and seas, became a concern in water management initially in Scandinavian countries and the United States and then spreading worldwide. This led to the establishment in 1991 of the European Community Urban Wastewater Directive (UWWD) which has set nitrogen and phosphorus standards for '*sensitive areas*' (Table 1.1), to be implemented throughout the Community by January 1999. '*Sensitive areas*' are defined as natural freshwater lakes, estuaries or coastal waters, which are, or may become eutrophic, or surface waters used for the abstraction of drinking water which may potentially contain more than the 50 mg nitrate l^{-1} which constitute the limit set by European Community. Wilson *et al* (1996) stated that for works discharging into such waters, and serving

over 10,000 pe ('*population equivalent*'), effluents must comply with the values for concentration or percentage reduction of total P and/or total N given in Table 1.1. A sum of £10-20 billion has been cited as the cost to the UK industry of compliance with the European Directive (UWWD), a significant proportion of which would inevitably be for sewage treatment (House of Lords, 1991).

Table 1.1: Nutrient limits required by the UWWD for discharge into rivers in sensitive areas

Nutrient	*Population equivalent* (a)	Concentration (mg l^{-1})	Minimum percentage reduction (b)
Total phosphorus	10 000 - 100 000	2	80
	> 100 000	1	80
Total nitrogen	10 000 - 100 000	15	70 - 80
	> 100 000	10	70 - 80

(a) BOD from industrial effluents may be converted into '*population equivalents*' units, using a value of 60 g of BOD per capita per day as the standard value (Rowe and Abdel-Magid, 1995).

(b) reduction in relation to the load of the influent

1.1.2 Sewage and basic treatment processes

Sewage is a dilute mixture of domestic waste, industrial (trade) waste, infiltration from the subsoil, and to a greater or lesser extent, runoff of surface water (Haworth, 1984). Its composition is extremely complex and varies considerably depending on the amount of water used per head of population, the degree of infiltration of subsoil water and the nature and proportion of trade effluents present.

The main objective of sewage treatment is to reduce the *strength* (concentration of pollutants) to a sufficient degree to allow safe discharge into natural waters without causing a nuisance or offence (Mason, 1991). For practical purposes, the impurities

can be divided into three groups: i) substances suspended in the liquid; ii) substances dissolved in the liquid and iii) extremely fine, colloidal substances (The Institute of Sewage Purification, 1960).

There are four different stages which may be used in the treatment of sewage, depending on the quality of the effluent required: i) *Preliminary treatment* involves screening for large particles, maceration and removal of grit and the separation of storm flows; ii) *Primary treatment (sedimentation)* is the process where the suspended solids are separated out as a sludge; iii) *Secondary treatment* is the process where dissolved and colloidal substances are oxidised in the presence of microorganisms; and iv) *Tertiary treatment* (often referred to as *'polishing'*) is used when a very high quality effluent is required. It may involve further reduction in biological oxygen demand (BOD), suspended solids (SS), bacteria, specific toxic compounds or nutrients (Mason, 1991).

However, the type of treatment to be used for wastewater purification will depend on the objectives for the quality of the receiving water and the amount of dilution which is available for that water. For example, preliminary treatment only may be given for effluents being discharged in the sea, whereas tertiary treatment may be required if water is needed for potable supply downstream of a discharge. In addition, nutrient removal is usually achieved in tertiary (advanced) wastewater treatment. In the following sub-sections, a brief overview of the conventional systems for removal of nutrients is presented, followed by an outline of alternative, emergent macrophyte-based (constructed wetland) systems for treating the wastewater from small communities.

1.2 Phosphorus removal in conventional systems

1.2.1 Forms of phosphorus

The common forms of phosphorus in wastewater are orthophosphate (PO_4^{3-}), polyphosphates (polymers of phosphoric acid) and organically bound phosphates. The

latter two forms gradually hydrolyse in water to the soluble ortho form (Hammer, 1986) and, therefore, it could be said that orthophosphate presents the principal form of phosphorus in wastewater (Horan, 1990; McEldowney *et al.*, 1993). The major sources of phosphorus (P) in domestic wastewaters are from human excreta (typically 50 - 65 % of the total P) and synthetic detergents (30 - 50 %), with a typical P concentration of 10 - 30 mg l^{-1} (Horan, 1990).

1.2.2 Phosphorus removal

The two basic phosphorus removal processes are chemical removal and biological removal (Cooper *et al.*, 1994). Chemical P removal is based on the addition of metal salt or lime to the wastewater, causing precipitation of insoluble phosphate which settles in the sedimentation tank (IWEM, 1994; Cooper *et al.*, 1994; Harper, 1995). The most common metals used are iron (either ferric, Fe^{3+}, or ferrous, Fe^{2+}), aluminium (Al^{3+}) and calcium (Ca^{2+}). The salts that are most frequently employed are ferric chloride ($FeCl_3$), ferric sulphate ($Fe_2(SO_4)_3$), ferrous chloride ($FeCl_2$), ferrous sulphate ($FeSO_4$), alum ($Al_2(SO_4)_3 \cdot 18\ H_2O$ and lime ($Ca(OH)_2$) (Ramalho, 1977). The reactions take place as follows:

$$Fe^{3+} + PO_4^{3-} \rightarrow Fe\,PO_4 \downarrow$$

$$Al^{3+} + PO_4^{3-} \rightarrow Al\,PO_4 \downarrow$$

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2 \downarrow$$

Waste pickle liquor from the steel industry (a mixture of ferrous sulphate and ferrous chloride) may also be used, but it requires pH adjustment with sodium hydroxide or lime (Hammer, 1986). Lime has been used less frequently, compared with metal salts, because of the substantial increase in the mass of sludge due to the simultaneous production of calcium carbonate (Cooper *et al.*, 1994). The precipitants can be added at any stage of the sewage treatment process: prior to primary sedimentation (pre-precipitation), to the aeration tank during the activated sludge stage (co-precipitation)

or during the clarification process (post-precipitation) (Horan, 1992; Tchobanoglous and Burton, 1991) (Figure 1.1, below):

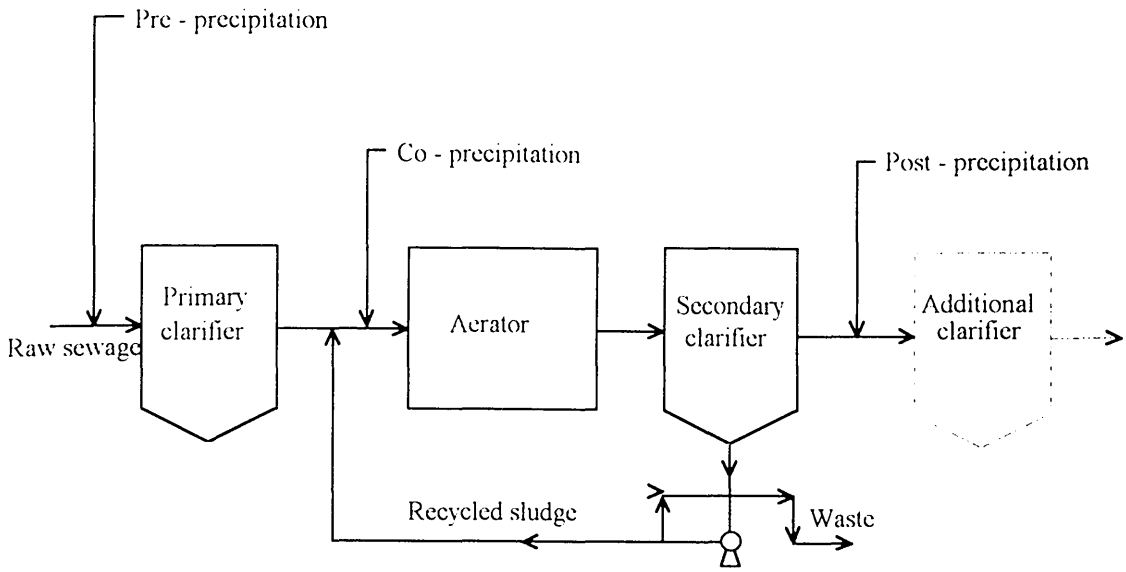


Figure 1.1: Alternative precipitation operations for phosphorus removal. Source: Ramalho (1977).

The chemical application rates are influenced by the engineering design, which includes mixing, flocculation and sedimentation characteristics, contact time, sludge age, residence time and recycling ratio. They also depend on wastewater characteristics (influent P concentrations, pH, total organic carbon, temperature), flow rate, hydraulic loading and the chemical used (Yeoman *et al.*, 1988). The choice of chemical used can be affected by several factors, the most important being pH, because it affects the ability of the sludge to settle. Precipitation of ferric phosphate is optimal at pH 5.0, of aluminium phosphate at pH 6.0, and of calcium phosphate at pH 9 and above (IWEM, 1994). Removal efficiencies commonly achieved are 90 % with Fe^{3+} (dosage 10 mg l^{-1}), up to 95 % with Al^{3+} (dosage 200 to 250 mg l^{-1}) and approximately 80 % using Ca^{2+} at a dosage of 700 mg l^{-1} (Ramalho, 1977). The relative merits of different processes and chemicals have been reviewed by Yeoman *et al.* (1988) and Balmer and Hultman (1988).

Biological removal processes rely on the phenomenon of 'luxury uptake' of phosphorus, which occurs when activated sludge undergoes a period of anaerobiosis followed by aeration (Horan, 1992). The components of an activated sludge plant are the aeration tanks in which the biological oxidation takes place, the settling tanks for the recovery of the activated sludge, and the system of pipes and pumps to return the activated sludge to the inlet end of the aeration tank (White, 1978) (Figure 1.2).

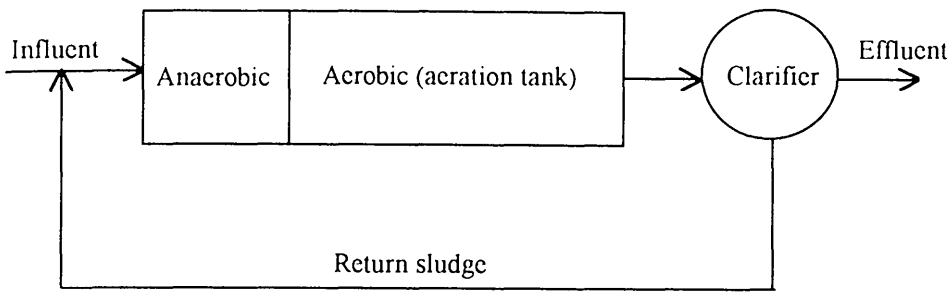


Figure 1.2 : Activated sludge system for biological phosphorus removal. Source: Stensel (1991).

Under anaerobic conditions sludge microorganisms which are deprived of both oxygen and nitrate excrete short chain fatty acids (formate, acetate, butyrate), which are then taken up by the bacteria of the genus *Acinetobacter*, which use them to synthesise an intracellular polymer, poly-β^- hydroxybutyrate (phb). This process requires energy which is obtained from the breakdown of the another intracellular polymer, polyphosphate. This reaction is associated with the release of phosphate into mixed liquor (solution). When *Acinetobacter* is exposed to aerobic conditions, the reverse reactions occur: phb is being degraded to produce energy which is then used to take up phosphate from the solution and synthesise polyphosphate. The phosphate taken up aerobically is in excess of that removed anaerobically and consequently phosphate is removed from the wastewater as a phosphate-rich sludge (Horan, 1990; IWEM, 1994). There is a variety of reactor configurations based on anaerobic and aerobic reactors with internal recirculation of reactor contents and recycling of returned sludge to the anaerobic zone. Biological removal processes in which P is removed in the sludge are referred to as '*mainstream processes*' and they are capable of achieving P effluent concentrations of 0.5 mg l^{-1} (Horan, 1992).

Biological P removal can also be achieved in stabilization ponds. In these systems, oxygen is provided by natural surface aeration and algae during photosynthesis. Oxygen released is then utilized by bacteria for aerobic degradation of organic matter. Stabilization ponds can yield relatively high P and N removal, provided that light and temperature conditions are favourable to the growth of algae. During the summer, removal of about 80% can be obtained, but during winter the efficiency of the systems can drop to only 20% or less (Ramalho, 1977).

If the combination of biological and chemical processes is used, the phosphate-rich supernatant is dosed with lime to precipitate phosphate. The phosphate-depleted sludge can then be returned to the aerobic reactor where it is exposed to the luxury uptake of P once again. This option is known as the *Phostrip* process and represents an example of a '*sidestream process*' (Tetreault *et al.*, 1986; Sedlak, 1991).

1.3 Nitrogen removal in conventional systems

1.3.1 Forms of nitrogen

Domestic wastewater contains nitrogen, either organically bound as protein and nucleic acids, as urea or as the ammonium ion (NH_4^+), with nitrites and nitrates rarely being present (Horan, 1990). Ramalho (1977) suggested that NH_4^+-nitrogen represents 50-60%, organic nitrogen 40-60% and nitrites and nitrates 0-5%, while Culp *et al.* (1978) stated that 90% of the nitrogen content of raw domestic wastewater is commonly in the form of ammonia or compounds from which it is readily formed. The total nitrogen content of wastewater is often referred to as the Total Kjeldahl Nitrogen (TKN), according to the technique by which it is determined. However, it is important to emphasise that TKN measurement gives the amount of organic N plus ammonium N, but excludes most of the nitrate-N which is lost during digestion (Rowell, 1994). If it is desirable to include nitrate - N the modified salicylic-sulphuric acid procedure is used (Bremner, 1965). The major source (80%) of TKN is urine from households (Laak, 1986).

1.3.2 Nitrogen removal

Nitrogen may be removed by either chemical (ammonia stripping, selective ion exchange) or biological means (Cooper *et al.*, 1994). Ammonia stripping is a process which consists of adjusting the pH of the wastewater to a value above 10 (usually using lime), followed by air stripping of the ammonia in a stripping tower (at pH > 10 nitrogen is present as NH_3) and then exposing it to granular activated carbon to adsorb dissolved organics (Ramalho, 1977). Selective ion exchange can be accomplished by passing the wastewater through the bed of the ion-exchanger which exhibits a high selectivity for the ammonium ion over other cations commonly present in wastewater (Sedlak, 1991). According to Tchobalogonous and Burton (1991), clinoptilolite, a naturally occuring zeolite, is one of the most suitable natural ion exchangers.

Biological removal of nitrogen involves three basic processes: i) *synthesis* - incorporation of nitrogen into the microbial mass as a result of cell growth; ii) *nitrification* - conversion of the ammonia and organic nitrogen to nitrate through oxidation by nitrifying organisms; iii) *denitrification* - conversion of the nitrate to nitrogen gas by denitrifying organisms (Horan, 1990; Hammer, 1986). The latter two processes are described in detail in Sections 1.7.5.3 and 1.7.5.4. All the various biological removal systems which are currently available use these processes. The methods of their incorporation into wastewater treatment are illustrated in Figure 1.3. They may be grouped according to the method of denitrification: i) denitrification in a separate unit process, referred to as 'separate stage denitrification' (Figure 1.3.a and b); ii) combined carbon oxidation, nitrification and denitrification, which is referred to as the 'single-sludge' process (1.3.c). A similar approach is used to accomplish nitrification. Separate stage nitrification (Figure 1.3.a) involves the use of two biological processes in series, whereby the first one removes carbonaceous biological oxygen demand (BOD) and the second one is used to nitrify the low BOD effluent from the first process. When a combined carbon oxidation and nitrification system is used ('two-stage' or 'two-sludge' process), the first stage accomplishes BOD removal and nitrification, while the second stage denitrifies the nitrate nitrogen contained in the

effluent after the first stage. Therefore, in either of these processes, denitrification takes place in a separate unit process following carbonaceous BOD removal and nitrification (Sedlak, 1991).

The selection of nitrogen removal by conventional systems, their cost effectiveness and the potential environmental impacts which must be taken into consideration are discussed by Culp *et al.* (1978) and more recently by Tchobalogonous and Burton (1991).

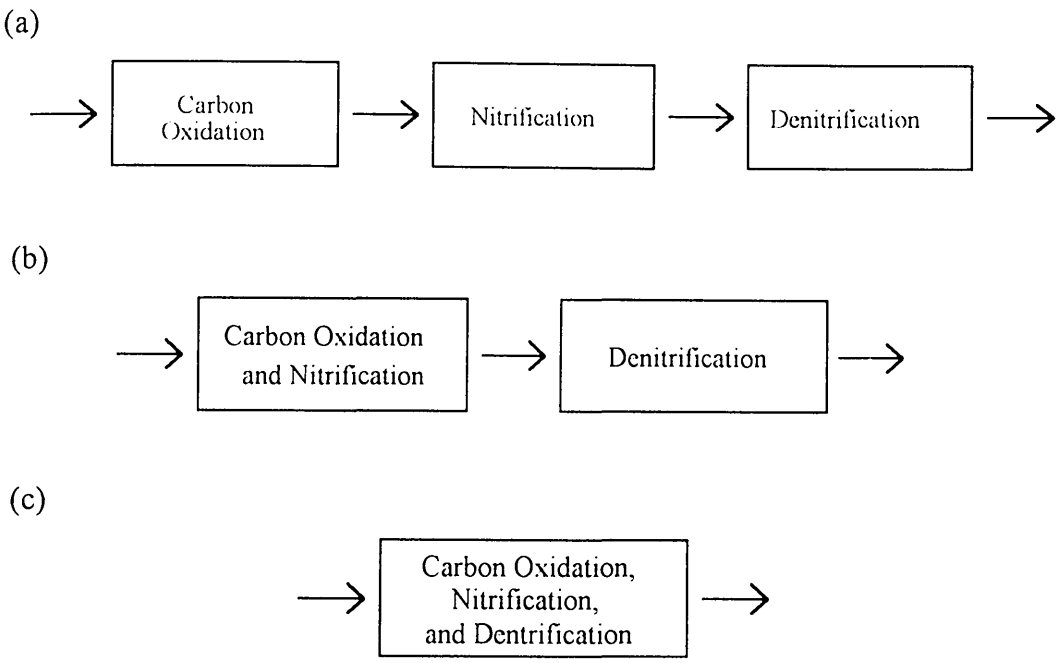


Figure 1.3: Three major approaches to biological nitrogen removal: (a) Separate Stage Carbon Oxidation, Nitrification, Denitrification; (b) Combined Carbon Oxidation and Nitrification, Separate Stage Denitrification; (c) Combined Carbon Oxidation, Nitrification and Denitrification. Source: Daigger and Polson (1991).

1.4 Disadvantages of conventional treatment systems for P and N removal

The common feature of conventional systems for P and N removal is that waste water is treated rapidly in highly managed, energy-intensive environments with short residence times. The systems are also expensive and require some degree of expertise to operate. For example, the proper functioning of the chemical treatment systems depends on the regular supply of chemicals and their correct dosage. In addition, they

are sensitive to the supply of energy because of the dosing pumps and have to cope with the disposal of large volumes of sludge (Horan, 1992). Biological treatment systems require less control of the equipment than chemical ones. On the other hand, maintaining the biological process itself may be more difficult, especially for activated sludge units where the separation of sludge represents the critical part (Winkler, 1981). Although the activated sludge units are often regarded as having a relatively low initial cost and a low requirement for land, they demand a substantial power supply and can be a source of noise and aerosol sprays (Lowe, 1990).

Furthermore, because of their operational costs, size and structural configuration, conventional systems for P and N removal are not an applicable option for wastewater treatment in small communities (Tchobanoglous and Burton, 1991; Somlyody, 1994).

1.5. Wastewater treatment needs for small communities

A small community is defined as one with an upper population limit of 2,000 (WHO, 1985). Such communities often have limited technical resources and therefore a low level of facilities in both water supply and sanitation systems. They may contain polluting agricultural processing activities or even small-scale industrial activities. Because of their size, small communities are exposed to a variety of problems that make the provision of wastewater treatment facilities very difficult. According to Tchobanoglous and Burton (1991), the principal problems are stringent discharge requirements which are the same for both large and small communities. This puts small communities under big economic constraints in the form of high per capita costs, caused in part by the population often being widely spread and difficult to access. In addition, small communities usually have limited finances available, due to lower household incomes and residential tax base and in most cases the treatment techniques are too complex for the educational level of the operators.

Therefore it is of the utmost importance to develop effective low-maintenance wastewater treatment for small communities. According to Lowe (1990) the following features are desirable, and some are essential: reliable and effective sewage

treatment to the desired standard throughout the year; no power requirement; minimum maintenance which, when needed, to be undertaken by unskilled operators; the production of as little sludge as possible; attractive appearance; no environmental nuisance such as noise, odour or insects; the ability to cope with daily as well as yearly fluctuations of flow.

A lot of work has been undertaken during the past two decades to develop alternatives to conventional systems which place the minimum environmental and economic pressure on small communities. Most of these are based on natural ecosystems, regarded as 'low technology' wastewater treatments.

1.6 Wetlands

The capability of wetlands for the disposal and renovation of wastewater has been demonstrated in a variety of natural wetland types across the United States as well as in western Europe (Best, 1985; Reed and Bastian, 1987; Hammer, 1989). According to Chan *et al.* (1981), there are four main functions of wetlands which make them potentially attractive for wastewater treatment: dispersion of surface waters over a large area; physical sorption of pollutants onto surface areas of the wetland soils and organic litter; uptake and metabolic utilisation by plants; transformation and utilisation of the elements by micro-organisms.

However, although reports on the effectiveness of wetlands for removing P and N have been encouraging, many questions about their sorption capacity, uptake rates and long term efficiency remain unanswered (Richardson and Nichols, 1985). Furthermore, the extreme variety of characteristics of natural wetlands and the difficulty of understanding or predicting pollutant removal processes initiated the development of constructed wetlands (Richardson and Davis, 1987; Hantzsche, 1985).

1.7 Constructed wetland systems

1.7.1 Definition and historical background

Several different terms have been used among wetland scientists and in the literature to describe constructed wetland systems. Hammer (1992) defined *constructed wetlands* as wetlands which are intentionally created from non-wetland sites merely for wastewater or stormwater treatment, whereas *created wetlands* are formed from non-wetland sites aiming to produce or replace natural habitats. Until the late 1980s the term *artificial wetlands* was used in the literature but according to Brix (1994 a) the term *constructed wetlands* is preferred by most wetland scientists today.

The historical development of the use of constructed wetland systems (CWS) for water purification worldwide has been reviewed by Brix (1994 a). The early works by Seidel (1966) inspired Kickuth (1977; 1982) to develop the concept of the 'Root-Zone Method' (German: Wurzelraumentsorgung). A root-zone design is basically a constructed wetland with subsurface horizontal flow (see section 1.7.2). It consists of a rectangular bed containing emergent vegetation, usually reeds (*Phragmites australis*) growing in soil (Brix, 1987; 1994 b). Kickuth (1982) claimed that the wastewater would penetrate through the soil and no surface runoff will occur. However, performance expectations for a root-zone design have not been attained, mainly because Kickuth (1977) predicted an increase in soil permeability with time (Brix and Scierup, 1989). In addition, the capacity of reeds to transfer oxygen to the rhizosphere is considered to be much less than claimed by Kickuth (Brix, 1993). (See Section 1.7.5.5).

The idea of the root-zone design was followed by extensive examination of both pre-existing natural wetlands and systems specially constructed for wastewater treatment for their purification performance (Hammer, 1989; Cooper and Findlater, 1990; Etnier and Guterstam, 1991; Moshiri, 1993). A typical arrangement of a CWS is presented in Figure 1.4. It consists of a basin, sealed to prevent percolation of effluent to the underlying soil and groundwater, and containing a bed matrix in which a stand of

aquatic plants is grown (Findlater, Hobson and Cooper, 1990). The objective of the engineering bed is to reduce greatly the concentration of pollutants during the passage of the effluent water through the bed. The major system components believed to function in the wastewater treatment processes are the soil (or other medium), the vegetation and the rhizosphere organisms.

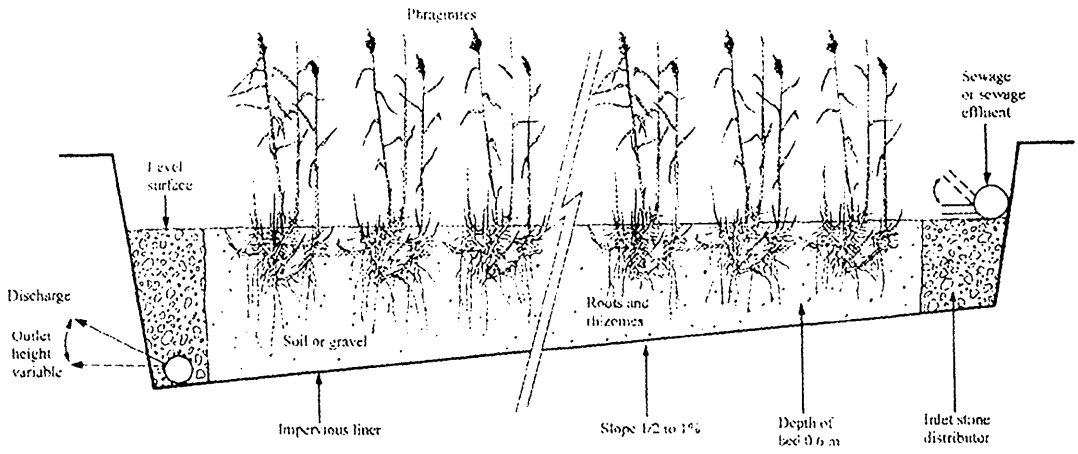


Figure 1.4: Cross-sectional area of a typical constructed wetland system. Source: Cooper (1993).

1.7.2 Types of constructed wetland systems

There are three basic types of constructed wetlands according to the life form of the dominating macrophyte in the wetland (Brix and Schierup, 1989; Brix, 1991; Brix, 1993):

i) *Free-floating macrophyte-based systems* (Species: water hyacinth, *Eichhornia crassipes*, and duckweed, *Lemna sp.*) can provide nutrient removal and upgrade the performance of conventional stabilisation ponds, mainly through incorporation into their biomass. They have been successfully applied in the tropics and subtropics, and their design, performance and operation has been reviewed by Brix (1993).

ii) *Submerged macrophyte-based systems* (Species: *Egeria densa*, *Elodea canadensis*) can be used as a final polishing step after primary and secondary treatment because the plants can only grow well in oxygenated water and therefore

the system cannot be used for the treatment of wastewater with a high content of biodegradable organic matter (Gumbricht, 1993; Brix, 1993).

iii) *Emergent macrophyte-based systems* (Species: common reed, *Phragmites australis*; cattail, *Typha latifolia*; bulrush, *Scirpus lacustris*; iris, *Iris pseudacorus*): there are three kinds, each with a different flow regime: *free surface flow*, *subsurface horizontal flow* and *vertical (non saturated) flow* (Figure 1.5).

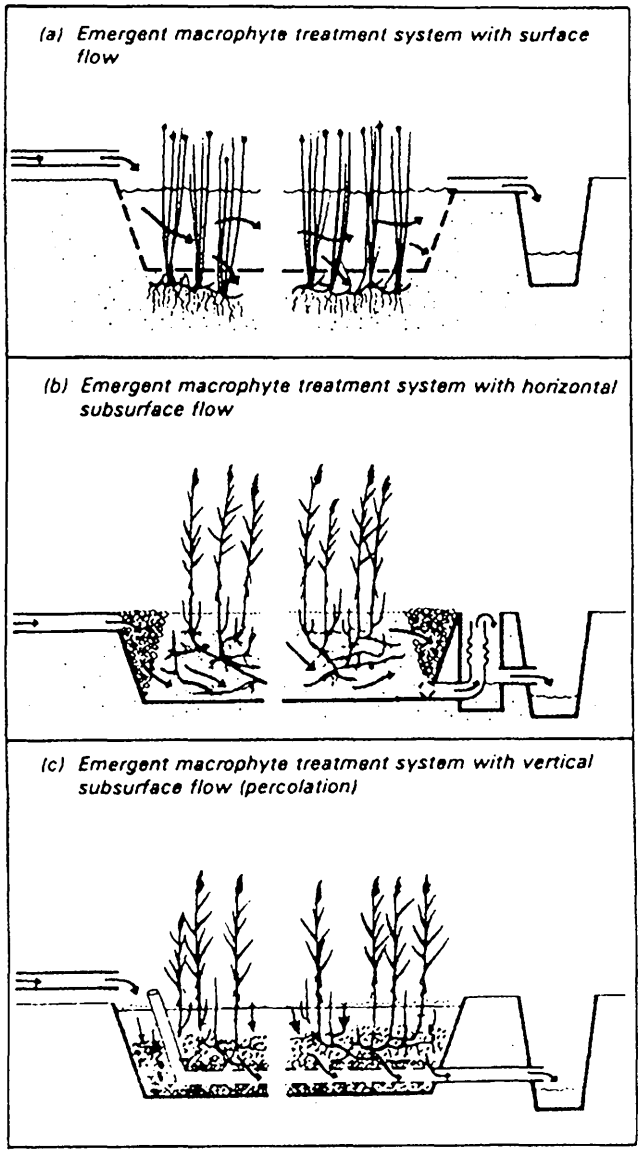


Figure 1.5: Schematic representation of emergent macrophyte - based wastewater treatment systems. Source: Brix (1993).

Free Surface Flow Systems (FWS) are flooded, the water surface is exposed to the atmosphere and the effluent flows at a relatively shallow depth. They are predominantly used in North America, characterised by large surface areas and low hydraulic loading (water flow rate divided by the wetland area) (Knight *et al.*, 1993). The Vertical Flow Systems (VF) design often consists of several beds laid in parallel, with wastewater usually applied at time intervals similar to those used with intermittent sand filters, and allowed to percolate through the medium (Brix, 1994 b). It is believed that intermittent loading provides oxidising and reducing conditions necessary to enhance nitrogen and phosphorus removal (Hill and Sawhney, 1981). The number of systems constructed with this type of design in Europe is increasing, but information on systems performance remains sparse (Brix, 1993).

With Subsurface Water Flow (SWF) systems the water level is maintained less than 5 cm below the surface (Forum, 1995). They are predominantly designed using the Root-Zone Method (section 1.7.1). Several hundred examples have been constructed - it is the predominant design in Europe and the system researched in this thesis.

1.7.3 Hydraulic design considerations

Because of the urgent need for data and information on the systems' performance, most of the studies to date have focused on actual measurements of what was coming into and out of the constructed systems. Theoretical pollutant removal models have been developed by several authors (Hammer and Knight, 1994; Kadlec, 1995; Reed *et al.*, 1995; Bavor *et al.*, 1995, Kadlec and Knight, 1996). Their form involves an exponential decrease in pollutant concentrations. The model can be expressed as follows:

$$q \frac{dC}{dx} = -k (C - C^*) \qquad (1)$$

where

q hydraulic loading rate defined as the ratio of the inflow (Q, $m^3\ d^{-1}$) and the surface area (A, m^2); x = fraction of distance from inlet to outlet; C = pollutant

concentration of the system (g m^{-3}); C^* = background pollutant concentration (g m^{-3}); k = first order area-based reduction rate constant (m d^{-1}).

Integrating Eq. (1) over the length of the wetland gives the equation:

$$\frac{Cx - C^*}{Ci - C^*} = e^{-k/q} \qquad (2)$$

where

Ci = inlet pollutant concentration of the system (g m^{-3}); Cx = pollutant concentration of the system at fractional distance x from inlet to outlet (g m^{-3}).

An alternative approach, based on the concept of water retention time has been formulated by Kadlec and Knight (1996):

$$\frac{Cx - C^*}{Ci - C^*} = e^{-k_v Tx} \qquad (3)$$

where k_v = first order volumetric reduction rate constant (d^{-1}); x = fractional distance through the wetland; T = retention time (days).

Hydraulic retention time (T) represents an important design and operational parameter for optimising performance of a wetland system with typical values ranging from 5 to 14 days for free water surface and 2 to 7 days for subsurface flow systems (Knight, 1994; Wood, 1995). In UK systems, the surface area required for secondary sewage treatment is usually 5 m^2 per population equivalent (pe) though it was estimated that it could be reduced to 1 m^2 pe^{-1} for tertiary treatment (Cooper and Green, 1995). The configuration of the systems should be such that it minimises channelling and short-circuiting and maximises contact between the wastewater and the substrate. In this regard, aspect ratio (length to width) plays an important role (Steiner and Freeman, 1989). While early designs were based on larger aspect ratios (4:1 to 10:1) because of familiarity with plug flow reactors and a lack of kinetic design information,

it is now thought that aspect ratios of 1:1 are more appropriate because they offer reduced construction costs and improved hydraulic control (Tchobanoglous, 1993; Buchberger and Shaw, 1995). Porosities of the systems usually range from 30 % for coarse gravels to 45 % for clay and silt (although in the later, the permeability is very low) (Watson *et al*, 1989; Reed, 1992). Most UK and European subsurface systems are built to a depth of 0.6 m at the inlet, with the outlet being slightly deeper to fit the slope (Cooper *et al.*, 1996). This choice is established because it is believed that beyond 0.6 m plant roots start to weaken, while shallower systems may suffer from freezing (Cooper *et al.* 1989).

Flow through fully saturated, fine-grained soils, sands and gravel is defined by Darcy's law:

$$Q = k\,A\,\Delta h/\Delta L \qquad (4)$$

where Q = flow of the system ($m^3\ d^{-1}$); k = hydraulic conductivity of a unit area of the medium perpendicular to the flow direction ($m\ d^{-1}$); A = cross-sectional area of the bed (m^2); $\Delta h/\Delta L$= hydraulic gradient of the flow system, expressed as a decimal fraction.

The cross-sectional area of the bed for a given flow is determined by the bed hydraulic gradient and hydraulic conductivity, both being essential parameters in the design of subsurface constructed wetland systems. The European Guidelines suggest that hydraulic conductivity (k) should be around 10^{-3} m s^{-1} (EC/EWPCA, 1990) and typical values for a variety of substrates (from clays to coarse gravels) are given in Table 1.2.

The slope of the beds is usually between 0.5 and 2 % (Steiner and Freeman, 1989). Despite these theoretical models of hydraulic design, there is no generally accepted consensus regarding optimal engineering design of CWS. Moreover, design is often based on a predictable or assumed set of conditions rather on real data (Bavor, *et al.*, 1995). For example, very few studies take into account the influence of geometric

configuration, aspect ratio, depth of water or type of media (Reed, 1991). Optimal design and operation of constructed wetlands are constrained because of the lack of data and understanding of the key mechanisms of pollutant removal processes (Bavor, *et al.*, 1995).

Table 1.2: Typical values for hydraulic conductivity (k) for different mineral substrates. Source: Cooper *et al.* (1996).

Soil texture	m s^{-1}
Fine to coarse gravel	10^{-3} - 1
Fine to coarse sand	10^{-7} - 10^{-2}
Karst limestone	10^{-4} - 10^{-2}
Sandstone	10^{-8} - 10^{-4}
Silt, loess	10^{-9} - 10^{-5}
Glacial till	10^{-12} - 10^{-4}
Unweathered marine clay	10^{-12} - 10^{-9}

1.7.4 Phosphorus removal by constructed wetland systems

Although there are few studies that outline the mechanisms controlling phosphorus retention capacity in freshwater wetlands (Howard-Williams, 1985; Richardson, 1985), different experiments have been conducted across the world in order to estimate the potential of both natural and constructed wetland systems to remove phosphorus from wastewater (Swindell and Jackson, 1990; Mann, 1990; Mann and Bavor 1993; Davies and Cottingham 1993; Gumbricht, 1993; Jenssen *et al.* 1993; Kadlec 1995; Bavor *et al.*, 1995). Results from their studies demonstrate that the removal of P occurs through substratum adsorption and chemical precipitation, plant and algal uptake, bacterial action and accumulation of organic matter (peat accretion) (Figure 1.6), but the exact contribution of each of these processes has still not been quantified (Hammer, 1989; Cooper and Findlater; Moshiri 1993; Richardson and Craft, 1993; Flaig and Reddy, 1995).

1.7.4.1 Substratum adsorption and chemical precipitation

Special attention has been paid to the mechanisms which occur within a substratum and it is agreed that there are several factors which influence these processes: Fe, Al and Ca content, redox potential (E_h) and pH (Fillos and Swanson, 1975; Nichols, 1983; Scholes *et al.*, 1986; Richardson & Davis, 1987). The role of iron, aluminium and calcium in the fixation of phosphorus by soil and sediments has long been recognised (Low and Black 1950; Kittrick and Jackson 1956; Hsu 1964) and since then numerous studies have been made in order to clarify the mechanisms involved in

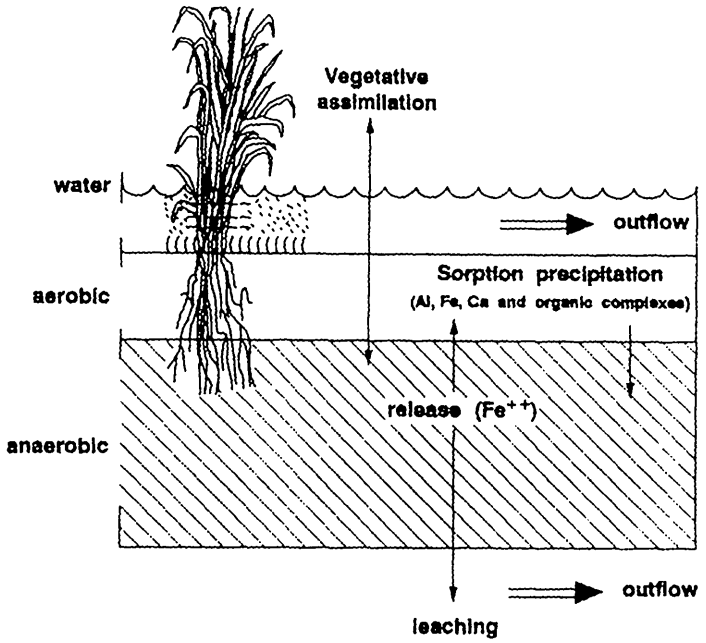


Figure 1.6: Generalized scheme of phosphorus transformation in wetland system. Source: Sharpley (1995).

phosphorus adsorption from soil solutions (Olsen and Watanabe 1957; Syers *et al.* 1971; Patrick and Khalid, 1974; Richardson, 1985; Cooke *et al*, 1993). Several researchers have demonstrated that the mechanism of phosphorus removal is mainly a sorption process attributed to a *gel complex* consisting largely of hydrated iron oxide (Shukla *et al.*, 1971; Williams *et al.*, 1971; Patrick and Khalid, 1974). Under anaerobic conditions, most of the active iron is in the Fe^{2+} form, often occurring as a ferrous hydroxide gel complex. In addition, anaerobic soils and sediments have much higher iron concentrations in the solution (approximately 40 to 80 mg kg^{-1}) compared

to less than 1 mg kg^{-1} in aerobic soils, and a much greater amount of Fe adsorbed on the exchange complex (Patrick and Khalid, 1974). Williams *et al.* (1971) and Richardson (1985) suggested that the most important mechanisms are *ligand exchange reactions*, by which phosphate displaces water or hydroxyls from the surface of hydrated ferrous and aluminium oxides to form extremely stable monodentate and binuclear complexes within the co-ordination sphere of the hydrous oxide (Parfitt *et al.*, 1975).

Even though the oxidation state of P is unaffected by redox reactions, redox potential (E_h) is significant because of Fe reduction. The form of Fe-P known as reductant-soluble phosphorus (RS-P) is especially important in wetland systems. It is a poorly crystalline Fe compound which is stable under oxidising conditions, but releases adsorbed P and occluded P (inorganic P present as orthophosphate ions within the matrices of P retaining components) when the Fe^{3+} (ferric) form is reduced to the Fe^{2+} (ferrous) form following submergence (Gambrell and Patrick, 1978). Therefore, this sediment pool may release a large amount of P into the solution under flooded conditions, i.e. if a material high in RS-P is used as a substrate, it may result in increased effluent P levels (Patrick and Khalid, 1974; Faulkner and Richardson, 1989). On the other hand, a decrease in redox potential may also result in an increase in P sorption capacity due to the transformation of crystalline Al and Fe minerals to the amorphous form, which have a greater surface area and more sorption sites due to their larger number of singly co-ordinated surface hydroxyl ions (Nichols, 1983; Richardson and Craft, 1993).

Interaction of pH and E_h also influences P transformations in wetland soils. Although Eh controls Fe^{3+} reduction, pH controls dissolution and subsequent precipitation of reduced compounds (Cooke *et al*, 1993). In acid soils, inorganic P is adsorbed on hydrous oxides of Fe and Al and may precipitate as insoluble Fe-phosphates (Fe-P) and Al-phosphates (Al-P). Precipitation as insoluble Ca-phosphates (Ca-P) is the dominant transformation at pH greater than 7 (Richardson and Craft, 1993).

Despite the pathways of P transformations in wetland soils having been established, the substrates chosen have disappointed for a number of reasons (Cooper and Hobson, 1989). For example, in the mid-1980s, following a proposed Kickuth design, systems which were built in Germany and Denmark used soil (Hammer, 1989; Cooper and Findlater, 1990). However, many of these systems suffered an occurrence of overland flows and insufficient contact between wastewater and substrate, due to the low hydraulic conductivity (Brix and Schierup, 1989), and some of them had problems with erosion and poor reed growth (Cooper and Hobson, 1989). Following these bad experiences, gravel was introduced as a substrate in some systems in San Diego, California (Gersberg *et al.*, 1986), South Africa (Wood, 1990), Australia (Mann, 1990; Mann and Bavor, 1993) and Great Britain (Cooper and Findlater, 1990). This was based on the opinion that, with its coarse structure, gravel would prevent channelling of the systems and enable better development of the roots and rhizomes (Cooper and Hobson, 1989; Cooper and Findlater, 1990; Moshiri, 1993). However, Mann (1990) pointed out that the overall contribution that gravel substrata can make to the overall phosphorus removal efficiency by CWS has not been extensively examined. After a two-year investigation of a large-scale CWS, he indicated that significant P removal can take place and suggested that the selection of a gravel substratum should be based on a number of physical and chemical characteristics, such as: particle size distribution; hydraulic conductivity; pore size; shape of gravel; physical friability (disintegration); surface coating; phosphorus adsorption capacity; iron and aluminium oxide content; calcium content and anion and cation exchange capacities.

Wolstenholme and Bayes (1990) investigated four different substrates (fine pulverised ash, coarse pulverised ash, gravel quarry rejects and pea gravel) for a CWS at Valleyfield, Fife, and concluded that these substrates were not suitable for long term P removal from wastewater.

Different attempts have been made to improve P removal capacity. For example, Steiner and Freeman (1989) proposed adding aluminium and iron, while Willadsen *et al.* (1990) recommended the use of lime. Jenssen *et al.* (1993) suggested the use of an

industrially processed light expanded clay aggregate (LECA) because of its high phosphorus adsorptive capacity as well as high porosity and hydraulic conductivity. Since then this material has been widely used in experiments throughout Norway and Sweden (Zhu, 1997; Johansson, 1997). However, the cost-effectiveness of such systems has to be examined due to the use of energy in the production of this substrate.

The biggest problem in finding the optimal substrate for P removal lies in the fact that P accumulation in a wetland is a finite process and, once saturated, the substrate has to be replaced (Hiley, 1995). In addition, the materials are often placed in a CWS without investigation of their physical and chemical properties prior to construction (Mann 1990; Mann and Bavor 1993). Therefore, the most appropriate material to be used has yet to be found.

1.7.4.2 The role of emergent vegetation

The presence of emergent macrophytes in CWS has several important functions which support P removal mechanisms. Their indirect role lies in physical effects such as reducing the current velocities of water, which creates conditions for the filtering and settling of inorganic and organic matter as well as diminishing the risk of erosion (Brix, 1997). Plant cover has an insulation effect which is very important for wetland performance during winter, especially in temperate areas (Jenssen *et al.*, 1993; Brix, 1997). Most importantly, the roots and rhizomes which are buried in the wetland substrate increase the available surface area for attached growth of micro-organisms (Nichols, 1983; Brix, 1997) and precipitation reactions (Peverly *et al.*, 1995).

Biological uptake of P by emergent macrophytes varies between 30 and 150 kg P ha^{-1} y^{-1} (Brix, 1997). Most of the P is stored in the roots and dead material and thus only 2.5 to 12 kg P ha^{-1} y^{-1} is removable by harvesting (Howard-Williams, 1985; Hurry and Bellinger, 1990). This is generally insignificant when compared to the loadings of wastewater to the constructed wetland (Brix, 1994 b). Harvesting is a labour-intensive process and may even damage the performance of the CWS if applied in the

wrong way (Suzuki *et al.*, 1989). In addition, Harrison *et al.* (1988) pointed out that the summer harvesting of emergent macrophytes (in particular reeds) can considerably diminish growth in the following season. If the wetlands are not harvested, 35-75 % of the P that has been incorporated into the plant tissue will be returned to the water by decomposition processes (Richardson, 1985; Brix, 1997).

1.7.4.3 The role of algae

There are few studies which have investigated the role of algae in wetland systems (Wetzel, 1975; Kadlec, 1987; Swindell and Jackson, 1990). Kadlec (1987) stated that there are three main forms of algae which contribute substantially to wetland biomass production: epiphytes - which grow attached to the plants; the epipelon, growing on or in the surface layers of the litter and bottom sediments; and filamentous algae which can sometimes form extensive mats. Howard-Williams (1985) and Harrison *et al.* (1988) suggested that algae can take up significant amounts of P. However, because algae have a much shorter life span than most macrophytes this storage is largely temporary and is released as the algae decompose in autumn and winter (Kadlec, 1987; Backai, 1993).

1.7.4.4 Bacterial action

Very few studies have investigated the role of bacteria in P removal by CWS (Howard - Williams, 1985). Bacteria can assimilate P in their cell structure, but once a steady-state of biomass is reached within the bed no further removal of P will occur (Richardson and Marchall, 1986; Davis and Cottingham, 1993).

1.7.4.5 Peat accretion

While plant (1.7.4.2), algal (1.7.4.3) and bacterial uptake (1.7.4.4) represent short term P removal processes, long term removal is dependent on substrate adsorption (1.7.4.1) and peat accretion rates (Bavor *et al.*, 1995; Kadlec, 1995). In their review on mechanisms controlling P retention in wetlands, Richardson and Craft (1993)

suggested that the efficiency of any wetland to store P on a long term basis is determined by the annual peat or soil accretion rate multiplied by the net increase of P stored by these processes each year. In addition, they stated that, on average, the permanent storage of P is 0.5 g m^{-2} y^{-1}.

1.7.4.6 Systems performance

Cooper and Boon (1989) commented that P removal was not the objective of many CWS designs. Results from several studies showed a varied performance in a range of 30 to 90% depending on the strength of wastewater entering the system, systems design and loading rates (Richardson and Davis, 1987; Faulkner and Richardson, 1989).

For example, in monitored systems which had been receiving well treated effluent (P concentrations of 1.0 mg l^{-1} or lower) for more than 4 years, typical removal efficiencies were somewhat higher, between 60 and 90% (Bavor *et al.*, 1995), while Tchobanoglous (1996) observed removal rates of only 10 - 40% for subsurface flow systems with phosphorus inputs in the range of 7 to 10 mg l^{-1}. In addition, Knight *et al.* (1993) presented average treatment efficiencies of 55% based on operational data from 69 free water wetland systems and 15 vertical or horizontal subsurface systems.

The processing efficiency of added P among constructed wetland systems varies considerably, depending on application rates, with 65-90% removal efficiency at loading rates of less than 5.0 g m^{-2} y^{-1}. The efficiency decreases to 30-40% or less when P loadings are greater than 10-15 g m^{-2} y^{-1}. Also, it declines sharply after several years of cumulative P additions (Faulkner and Richardson, 1989; Bavor *et al.* 1995). Hiley (1995) pointed out that the removal rate of 1.9 t P $ha^{-1}y^{-1}$, which represented 60% of the applied load, by pulverised fuel ash in the Valleyfield CWS (Wolstenholme and Bayes, 1990) was decreasing after 2 years in operation. Mann (1990) reported that between 60 and 80% of the load applied to a CWS in Richmond, Australia containing a gravel substratum was removed within the first few months of

operation. However, he later concluded that this system was inefficient in P removal after a two-year trial (Mann and Bavor, 1993).

Overall, there is a wide range in P removal efficiency among wetlands at lower input levels (< 10 g m^{-2} y^{-1}), indicating a greater dependence on P transformations within the wetland and emphasising the importance of substrate type for P removal from wastewater.

1.7.5 Nitrogen removal by constructed wetland systems

The mechanisms influencing nitrogen transformations in wetland systems involve the interaction of mineralising, oxidising and reducing processes which transform nitrogen into gaseous forms which can escape (volatilize) to the atmosphere (Faulkner and Richardson, 1989;.Hammer and Knight, 1994). The mechanisms are presented in Figure 1.7, below:

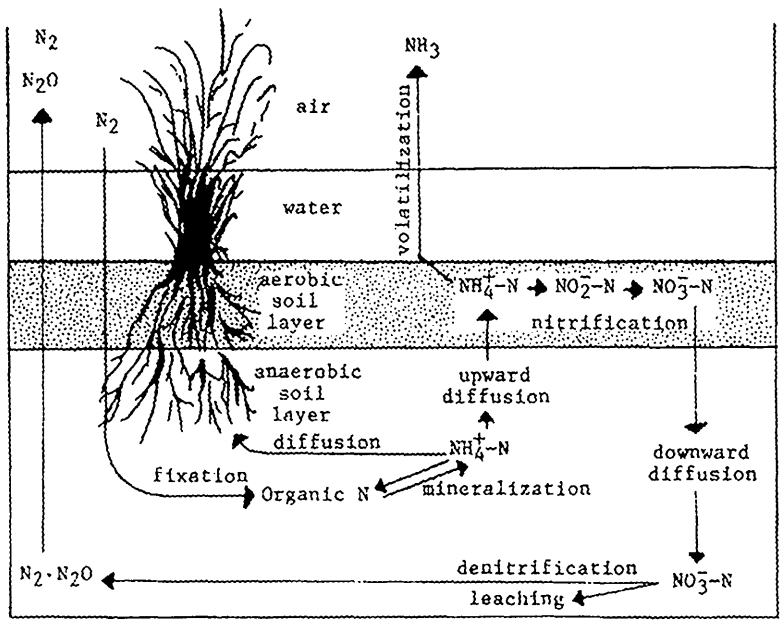


Figure 1.7: N transformation within the wetland system. Source: Gambrell *et al.* (1991).

1.7.5.1 Ammonification

Organically bound nitrogen in the form of proteins, amino acids and urea is

mineralised to ammonium N through the process of *ammonification* (Reddy and Patrick, 1984; Gumbricht 1993). The breakdown of organic compounds and the consequent mineralisation of N proceeds at a much slower rate in anaerobic than in aerobic environments (e.g. Reddy and Patrick, 1984).

1.7.5.2 Ammonia volatilization

In alkaline conditions, ammonium N undergoes a chemical reaction resulting in the evolution of ammonia gas (NH_3), which can act as a removal mechanism for nitrogen in CWS (Reed *et al.*, 1988). The ammonium ions are in equilibrium with free ammonia gas according to the equation:

$$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+ \qquad (5)$$

The equilibrium is strongly affected by pH, so that as the pH increases more of the ammonium will be converted to unionised ammonia gas in solution. At 15 °C and pH 7 less than 0.3 % of the ammonical N is present as unionised ammonia, whereas at 15 °C and pH 9.5 this increases to almost 50 % (Russell, 1994).

For the equilibrium, the dissociation constant is:

$$K_a = \frac{a_{NH_3} \times a_{H_3O^+}}{a_{NH_4^+}} \qquad (6)$$

and $K_a = 9.25$ (Heslop and Jones, 1976).

1.7.5.3 Nitrification

Biological oxidation of ammonium N (NH_4^+) to nitrate (NO_3^-) is an oxygen-demanding process which takes place in two stages as a result of the activity of

chemoautotrophic bacteria of the genera *Nitrosomonas* ($NH_4^+ \rightarrow NO_2^-$) and *Nitrobacter* ($NO_2^- \rightarrow NO_3^-$) It takes 2 mol of O_2 to oxidise each mol of ammonium to nitrate (Reddy and Patrick, 1984; Green *et al.*, 1997).

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$$

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (7)$$

In a wetland system, nitrification takes place in the surface-oxidised sediment layer (Gambrell and Patrick, 1978; Reddy and Patrick, 1986), the overlying water (Reddy and Graez, 1981) and the root zone (Reddy and D'Angelo, 1997). Nitrifying organisms obtain their energy from the oxidation of ammonium and nitrite ions. The growth rate of *Nitrosomonas* is smaller than that of *Nitrobacter* and therefore nitrite accumulation should not occur in an aerobic environment unless *Nitrobacter* is inhibited. Since the conversion of ammonium to nitrate is an oxidation reaction, its rate of conversion depends on the oxygen supply to the bacteria (Gambrell and Patrick, 1978).

In wetland systems, the nitrification rate is influenced by temperature, pH, alkalinity of the water, microbial population and inorganic C source (Reddy and Patrick, 1984; Faulkner and Richardson, 1989). In temperate climates, soil nitrifier populations are highest during spring and lowest during hot, dry summers and in winter. At temperatures of less than 5°C and greater than 40°C nitrification rates are low, being optimal between 30 and 35°C. Nitrification decreases at pH < 6.0 and is negligible at pH < 5.0. In addition, in alkaline soils with high salinity NO_3^- production is inhibited because nitrifiers cannot tolerate such conditions (Hammer and Knight, 1994). Since the process of nitrification is dependent on the metabolism of nitrifying organisms, they must be present in adequate quantities to achieve the oxidation of ammonium N. Results from studies on flooded soils and sediments have shown that large numbers of

nitrifying organisms occur in the surface layers and decrease with depth (Payne, 1981; Davidson *et al.*, 1978). Reddy and Graetz (1981) demonstrated that the rate of nitrification depends on the availability of CO_2 in a wetland system, being higher when waste water columns are aerated with air containing CO_2, than when aerated with CO_2 - free air.

1.7.5.4 Denitrification

Denitrification is the major mechanism for N removal from wetlands (Seitzinger, 1990), as during this process nitrate is converted into nitrous oxide (N_2O) or molecular nitrogen (N_2). When oxygen is lacking and in the presence of an available organic substrate, facultative anaerobic bacteria (*Pseudomonas*, *Achromobacter*, *Bacillus*, *Micrococcus*) use NO_3^- instead of O_2 as the terminal exogenous H acceptor for their respiration (Reddy and Patrick, 1984; Gumbricht, 1993). The overall reaction can be presented as:

$$\underset{\text{(nitrate)}}{NO_3^-} + \text{organic carbon} \rightarrow \underset{\text{(nitrite)}}{NO_2^-} + \text{organic carbon} \rightarrow \underset{\text{(nitrogen gas)}}{N_2} + CO_2 + H_2O \qquad (8)$$

There are several factors which influence the rate of denitrification in wetland systems: absence of O_2; presence of readily available carbon; temperature; pH; presence of denitrifiers (Seitzinger, 1990; Reddy and Patrick, 1984). As nitrification takes place in the oxygenated areas of the wetland, NO_3^- then diffuses to the anaerobic areas when it gets denitrified. The rate of diffusion or lack of oxygen for nitrification can also limit denitrification (Nichols, 1983). Organic carbon compounds serve as electron donors and support the growth of denitrifying bacteria (Nichols 1983; Reddy and D'Angelo, 1997). The optimal temperatures for denitrification are between 25 and 65 ^oC (Hammer and Knight, 1994). Stanford *et al.* (1973) showed that the rate of denitrification increases 1.5-2 fold with a 10^oC rise in temperature. It also proceeds more rapidly in neutral to alkaline pH than under acid conditions.

Nichols (1983) reviewed the research and reported that the optimum pH for a denitrification reaction is between 6.0 and 8.5.

1.7.5.5 The role of emergent vegetation

The bed medium is continuously water-saturated (with anoxic sewage with a significant BOD) and therefore generally anaerobic. The most limiting factor for nitrogen removal is an adequate supply of O_2 which is necessary to sustain nitrification (section 1.7.5.3). In this regard, the ability of aquatic plants to translocate oxygen from the shoots to the roots, establishing an oxidised area in an otherwise reduced environment, represents the most important factor (Gersberg *et al.*, 1989; Cooper and Findlater, 1990; Brix, 1994 b; Green *et al.*, 1997).

The occurrence of a flux of oxygen into the rhizosphere of aquatic plants is well documented (Armstrong, 1964; Boon, 1985; Brix, 1993), but the results of experimental determinations of this flux are erratic, probably due to the different techniques used and seasonal variation in O_2 release rates (Brix 1993; Brix, 1997). For example, Lawson (1985) calculated a possible O_2 flux from the roots of *Phragmites australis* to be 4.3 g m^{-2} day^{-1}. Other authors estimated release rates to be 5-12 g m^{-2} day^{-1} (Armstrong *et al.*, 1990), 1 to 2 g m^{-2} day^{-1} (Gries *et al.*, 1990) and 0.02 g m^{-2} day^{-1} (Brix, 1990). Rates of leakage are reported to be highest in the subapical region of the roots and decrease with distance from the root-apex (Armstrong, 1979; Brix, 1997). It was also expected that oxygen release from *Phragmites australis* will be higher than that from other aquatic plants, due to the convective through-flow mechanism and venturi-induced convection which may significantly enhance transmission of O_2 by passive molecular diffusion (Brix, 1993). However, the quantification of O_2 release is still under debate. While Sorell and Armstrong (1994) demonstrated the importance of an external oxygen sink in measuring its release from the root system and concluded that previous values were underestimated, it is generally agreed that the oxygen supplied through the plant roots is insufficient to support nitrification (Reed and Brown, 1995; Green *et al.*, 1997).

Plant uptake of nitrogen may be considered as a temporary storage mechanism from which N may be released again following plant senescence unless removed by harvesting (Kadlec and Knight, 1996). However, Bavor *et al.* (1995) reported that harvested planted material accounted for only 5 to 16 % of the input nitrogen. In addition, Brix (1997) stated that nitrogen removal by emergent macrophytes is in the range of 200 to 2500 kg N ha^{-1} y^{-1} and that the amounts of nutrients that can be removed by harvesting are generally insignificant when compared to the wastewater loadings into the constructed wetland.

1.7.5.6 Systems performance

Biological nitrification/denitrification is usually the most significant nitrogen removal mechanism in constructed wetland systems. However, nitrogen removal rates vary considerably depending on the input loading rates, the type of wetland, presence of vegetation and the type of pre-treatment (Cooper and Findlater, 1990; Moshiri, 1993 Kadlec and Knight, 1996). Hammer and Knight (1994) reported that nitrogen removal rates up to 79% could be achieved for loading rates up to 1600 g N m^{-2} y^{-1}. In several systems in the USA, removals varied between 20 and 70% in subsurface and 40 and 75% in surface flow systems (Tchobanoglous, 1996). Also, it was suggested that nitrogen removal efficiency could be improved through introducing vertical systems employing intermittent loading which would enhance nitrification (Brix, 1993). Two such systems were constructed in Austria (Laber, 1997), with the highest removal rates (82% for inorganic N and 72% for total N) achieved by adding an external carbon source (methanol) for the denitrifying bacteria. Green *et al.* (1997) achieved removal loading rates as high as 19 g NH_4^+ - N m^{-2} d^{-1}, using a passive air pump with a potential of 9 mol O_2 l^{-1} of effluent treated.

Vegetated CWS in general show better removal efficiencies than unvegetated ones (Hammer, 1989; Moshiri, 1993). For example Gersberg *et al.* (1986) measured 94% removal by systems planted with bullrush (*Scirpus lacustris*), 78% by reeds (*Phragmites australis*) and 28% by cattails (*Typha latifolia*) as compared with only 11% removed by unvegetated ones.

1.7.6 Advantages of constructed wetland systems

One of the main advantages of CWS is that they can be constructed to provide the same basic hydraulic and vegetative functions as natural wetlands, but with a much greater degree of control. There are also advantages over conventional treatment plants. They have low capital costs because the construction of the system is simple and no mechanical or electrical equipment is needed. Maintenance costs are extremely low. Also, the relatively long retention times gives the system robustness and ability to cope with peak loadings, not present in conventional systems. When they are performing satisfactorily, a consistent effluent quality is produced. Solids associated with the incoming sewage accumulate, but are retained within the bed for a very long period of time and the organic particles are almost completely mineralised. Consequently, sludge production is considerably smaller than from conventional treatment plants. Also, the retention of the sludge within the bed, together with a constant supply of debris from emergent vegetation, provides a food source to maintain micro-organism populations on the occasions when there is no sewage load for extended periods of time. Therefore it is expected that such systems are able to regain their full removal capacity, which may enhance their longevity.

Constructed wetlands are generally attractive in appearance and compatible with rural surroundings (Lowe, 1990). They do not interfere with natural wetlands and therefore they are environmentally acceptable with some potential for wildlife conservation (Bucksteeg, 1990; Knight, 1997).

1.7.7 Disadvantages of constructed wetland systems

The main disadvantage in the use of constructed wetlands lies in the fact that the technology is still at the development stage, i.e. there is an obvious lack of understanding of the extent to which physico-chemical processes, plants, micro-organisms and algal uptake influence the pollutant removal and therefore the optimal design and operating criteria have not been established (Hammer, 1989; Moshiri, 1993). In addition, there is a lack of information on long-term performance of

constructed wetlands.

1.8. Objectives of the research

The advantages of CWS as a means of waste water treatment are outlined in Section 1.7.6. Since they were introduced as a possible technology for waste water treatment in the early 1980s, they have proved to be extremely efficient (up to 90%) in the removal of some of the pollutants, such as BOD and suspended solids. However, their efficiency in P and N removal has been erratic. It seemed likely that the general use of what was effectively an inert growth medium (substrate) such as gravel was potentially less effective than another material which itself might be capable of fixing phosphorus. Therefore, one of the objectives of this project was to investigate other possible substrates that were more effective for P removal, while also being cheap enough and sufficiently readily available to be a realistic option.

Following the selection of a suitable material, it was planned that constructed wetlands should be established, using this material, to investigate phosphate and (to a lesser extent, ammonium) removal from waste water. The chosen design was one employing horizontal subsurface flow.

Additional specific objectives were:

1) to investigate the flow regime and geometrical configuration of the nutrients within the subsurface flow CWS;

2) to examine the influence of redox potential (Eh), pH and temperature (t) on P and N removal mechanisms; and

3) to examine the contribution of plants (*Phragmites australis*) to P and N removal.

Chapter 2: Some physical and chemical properties of phosphate-removing substrates for use in constructed wetlands[1]

2.1. Introduction

The immobilisation of phosphate in constructed wetland systems occurs through a combination of processes: substratum adsorption, chemical precipitation, bacterial action, plant and algal uptake and incorporation into organic matter (Swindell and Jackson, 1990; Richardson and Craft, 1993; Mann and Bavor, 1993; Flaig and Reddy, 1995; see Section 1.7.4). Of these, the substrate may play the greatest role and it is important to select those substrates with the greatest potential for P removal. Such materials might include minerals with reactive Fe or Al hydroxide or oxide groups on their surfaces (Section 1.7.4.1), or calcareous materials which can promote Ca phosphate precipitation. They should also be suitably permeable, in order to prevent surface channelling of the CWS (Wood, 1995; Kadlec and Knight, 1995). In addition, they should be cheap and locally available in order to reduce the costs of CWS construction. This chapter describes investigations of a range of candidate substrates, all meeting the above criteria. The substrates were compared with respect to both physical and chemical properties, in order to identify the optimal substrate for P removal.

Measurements were made of elemental composition, pH, cation exchange capacity (CEC), hydraulic conductivity, porosity, specific surface area and particle size distribution. These measurements were complemented by studies of:

- phosphate adsorption capacity;
- investigations of the P saturation point;
- investigations of the suitability of the materials as a substrate for plant growth, and

[1] This chapter is based on a paper entitled ' Some physical and chemical properties of phosphate-removing substrates for use in constructed wetlands', submitted to *Water Research*.

- X-ray fluorescence spectrometric analysis of the substrates after passage of waste water over them.

2.2. Materials and methods

2.2.1. Materials

The seven materials chosen for the investigation of their physico-chemical properties were:

- *Bauxite*, a naturally occurring mixture of minerals rich in hydrated aluminium oxides and ferric oxides and low in alkali metals, alkaline earths and silicates. It is the raw material from which aluminium is mainly produced. The material used in this experiment was Ghanaian in origin, and obtained from Alcan Chemicals Europe, Burntisland, Fife.
- *Shale*, an argillaceous rock which is highly fissile and which splits readily into very thin laminae. The material used for experiments was greyish black in colour and was derived from the lower limestone group of the carboniferous system. It was obtained from Cultshill Quarry, Fife. It is quarried there by the Wemyss Brick Co. as a raw material for brickmaking.
- *Burnt oil shale* (BOS), widely available in central Scotland as the waste product from heating oil shale to produce mineral oil. During the retorting process the oil shales were heated to temperatures in excess of 500 ^{o}C, breaking down the original alumino-silicate structures.
- *Limestone*, composed largely of calcium carbonate ($CaCO_3$) in the form of calcite. The material used for experiments was obtained from the Middleton Lime Quarry, Midlothian.
- *Zeolite*, a hydrated aluminium-silicate mineral with the aluminium and silicon polyhedra linked by the sharing of oxygen atoms. Zeolites are characterised by an extremely open, three-dimensional lattice structure through which alkali and alkaline earth cations can readily diffuse.
- *Lightweight expanded clay aggregates* (LECA), formed by expanding special clay

minerals at high temperature to produce lightweight (300-400 kg m^{-3}) ceramic pebbles. The material used for experiments was obtained from the Clydesdale Trading Company, Lanark, who had imported it from Norway.

- *Fly ash*, an inorganic waste product from coal combustion, consisting mainly of spherical glassy particles of silica (SiO_2), alumina (Al_2O_3) and iron oxides (Theis and McCabe, 1978). The material used here was furnace bottom ash which has coarser particle size and hence higher permeability than fine fly ash, and originated from Longannet Power station, Fife.

2.2.2. Methods

2.2.2.1. Determination of elemental composition, pH, CEC, hydraulic conductivity, porosity, specific surface area, and particle size distribution

Elemental analysis of the substrates was carried out with an inductively coupled argon plasma spectrometer (ICAP 61E, Thermo Unicam, Mass, USA) using the aqua-regia ($HCl + HNO_3$) digestion method to produce a solution of the sample materials (DoE, 1986). The pH of each substrate was determined using a pH meter (model 701a, Orion, Cambridge, Mass, USA) by mixing 2 g of milled (< 2 mm) material to 20 ml of 0.01 M $CaCl_2$ (McLean, 1982). Cation exchange capacity was measured using the colorimetric method with methylene blue (MB) (Rhoades, 1982). From the number of 'equivalents' of MB adsorbed the concentration of cations exchanged in the solution was calculated and CEC determined.

Hydraulic conductivity was measured using a constant head permeameter (0.65 m). Acrylic plastic tubes with two different bores (cross-sectional areas of 0.009 m^2 and 0.0035 m^2 respectively) were used. The tubes were filled with the different substrates to a height of 0.65 m. Water was passed through them, using an upward flow to facilitate removal of trapped air (Taylor and Ashcroft, 1972). The hydraulic conductivity was calculated using Darcy's law:

$$Q = k A (\Delta H/\Delta L) \quad (1)$$

where Q = volumetric flow rate of the of the solution (m^3 s^{-1}); k = saturated hydraulic conductivity (m s^{-1}); A = cross sectional area of the tube (m^2); $\Delta H/\Delta L$ = hydraulic gradient of the flow system expressed as a decimal fraction where ΔH = the hydraulic head (m) and ΔL = the length of the column (m).

The porosities of the substrates were determined using the standard soil science procedure based on estimations of bulk density and particle density (Klute, 1986). Specific surface area was determined using the N_2 gas adsorption method. This involves measuring the amount of gas adsorbed at the boiling point of liquid N_2 at atmospheric pressure (77 °K or -196 °C) as a function of the relative pressure p/p^o, where p is the partial pressure of the gas being adsorbed and p^o is its equilibrium vapour pressure (Davis and Kent, 1990). Particle size distribution was measured by sieving each of the substrates through four different mesh sizes, ranging from 2.8 mm to 12.7 mm.

2.2.2.2. Determination of maximum phosphate adsorption capacity

A slight modification of a standard batch equilibrium technique (Nair et al., 1984) was used. Five different P solutions, ranging in concentration from 2.5 to 40 mg P l^{-1} (0.08 to 1.25 mM P as KH_2PO_4 in 0.01 M $CaCl_2$), were equilibrated for 24 hours by continuous shaking on a rotating shaker at constant temperature (21°C). Three drops of toluene were added to each tube in order to inhibit microbial activity. Suspensions were then centrifuged and the P remaining in the supernatant was determined using a standard colorimetric method (Black, 1965). Phosphorus adsorption maxima were determined from the linearized form of the Langmuir equation (Olsen and Watanabe, 1957; Tchobanoglous and Schroeder, 1985):

$$C/(x/m) = 1/ab + C/b \quad (2)$$

where C is the concentration of P in the solution at equilibrium (g m^{-3}); x/m is the amount of P adsorbed per unit weight of material (g kg^{-1}); a is the constant related to the binding strength of P on the material; b is the P adsorption maximum (g kg^{-1}).

2.2.2.3. Determination of the time required for substrate saturation

Three Perspex columns (inner diameter: 100 mm; height: 900 mm) were packed with each of the four substrates found to have the highest P adsorption capacities, giving a total of 12 columns. The columns were fed from below with a synthetic waste water solution (Appendix 1) containing 35-45 mg P l^{-1} (as KH_2PO_4) from a common reservoir, using a separate peristaltic pump for each column. This P concentration, double the level of the average P concentration of domestic waste waters (10-20 mg P l^{-1}), was set because of the time limitations of the experiment. The upward flow rate was chosen to ensure good contact between effluent and substrate. The pumps were set to operate for 10 minute periods six times per day, at a rate of 3 l hr^{-1}. The average contact time between the solution and the substrate was 12 hours. Samples of the outflow from each column were taken every second day and analysed for P content, using a standard ammonium molybdate method (DoE, 1980), to determine when the saturation of the substrates was reached.

2.2.2.4. Determination of plant growth in different substrates

Phragmites australis seedlings were obtained from Yarnigsdale Nursery Gardens, Warwick, England and grown in a greenhouse until they reached an average height of 0.3 m. They were then transplanted into the four substrates and grown for 6 weeks (mid August - end of September 1994). Samples of the plant material were taken prior to and at the end of the 6-week period, oven dried and weighed to determine the dry matter content. Concentrations of mineral elements were then determined using an inductively coupled argon plasma spectrometer (ICP) (DoE, 1986).

2.2.2.5. Examination of the substrate surfaces by X-ray fluorescence spectrometry (XRF)

In order to determine whether phosphate precipitation occurred during the column experiment (Section 2.2.2.3), three replicate samples of each substrate material were taken from the columns after the saturation point had been reached, cut into 10 - 30 mm sections and analysed using an X-ray fluorescence spectometry (XRF) technique. This technique is based on bombarding a sample substance with radiation from an X-ray tube. The chemical composition of the material is analysed by measuring the intensity of the diffracted radiation at different wavelengths by varying the angle of diffraction, θ, according to Bragg's law (Brindley and Brown, 1980). Analyses were carried out with a Philips PW1480 spectrometer.

2.3. Results

2.3.1. Chemical and physical analyses

Elemental analyses confirmed that all of the materials (except the limestone) were rich in Fe and Al, with concentrations ranging between 3×10^3 and 10^5 mg kg^{-1} (Table 2.1).

pH was neutral to alkaline for five substrates, with only shale and bauxite being significantly acid. CEC values fell into two groups, with BOS, zeolite, limestone and shale more than twice as high as the remainder. Hydraulic conductivity was generally between 10^{-3} and 10^{-4} m s^{-1}, although that of zeolite was much higher (2.94×10^{-3}) (Table 2.2). Porosity was lowest for limestone (33 %) and the highest for zeolite (54.4%). The specific surface area for LECA and fly ash could not be calculated because the range of the relative pressure for these two substrates exceeded the range (between 0.05 and 0.30) for which the equation used in the N_2 adsorption method is valid (Davis and Kent, 1990). Particle size distribution varied considerably among the substrates (Table 2.3), with LECA and limestone containing the biggest proportion of

large particles (> 12.7 mm, 70.2% and 61.7% respectively) and fly ash the largest proportion of small particles (<2.8 mm, 77.8%).

Table 2.1: Elemental analysis of substrates (mg kg^{-1}). Each value represents a mean of two replicates.

Element	Bauxite	Shale	BOS	Zeolite	LECA	Fly ash
P	500	741	1510	74	180	945
K	93	3200	3770	1.96×10^4	1360	650
Na	9.3	171	2120	335	390	593
Mg	2.8	8150	4210	3550	4040	3320
Al	1.16×10^5	2.73×10^4	2.88×10^4	4.37×10^4	9630	1.49×10^4
S	245	3750	493	25	3050	494
Cu	11.8	29	28	2.0	28	50
Mn	11.1	390	470	17.3	57.1	340
Zn	49.0	80	37	17.2	24.8	84
Cr	367	44	38.4	3.4	16.0	14.2
Fe	1.08×10^5	3.64×10^4	5.4×10^4	3560	1.37×10^4	2.18×10^4
Ni	37	85	53	4.5	38	42
Pb	218	69	70	30	21	28

Table 2.2: pH, CEC, hydraulic conductivity (Hyd. con), porosity, and surface area of substrates. Each value represents a mean of three replicates.

Substrate	pH	CEC (cmol kg^{-1})	Hyd con (m $s^{-1} \times 10^{-4}$)	Porosity (%)	Surface area (m^2 g^{-1})
Bauxite	5.9 ± 0.1	8.5 ± 1.3	5.9 ± 0.3	34.5 ± 2.8	6.8 ± 0.4
Shale	4.5 ± 0.1	19.4 ± 2.8	10.0 ± 0.7	37.7 ± 1.9	19.9 ± 1.6
BOS[a]	7.4 ± 0.2	23.3 ± 1.0	10.2 ± 0.3	40.0 ± 2.0	8.3 ± 0.3
Limestone	7.8 ± 0.1	22.8 ± 1.3	2.4 ± 0.1	33.0 ± 1.6	7.4 ± 0.5
Zeolite	6.5 ± 0.2	23.0 ± 1.1	29.4 ± 0.5	54.4 ± 1.0	31.4 ± 0.2
LECA[b]	8.2 ± 0.1	9.5 ± 2.0	7.0 ± 0.2	40.4 ± 2.9	ND
Fly ash	8.3 ± 0.2	9.3 ± 0.4	2.8 ± 0.3	45.3 ± 3.0	ND

(± SD; n = 7); [a] BOS = Burnt oil shale; [b] LECA = Light expanded clay aggregates ND: not determined

Table 2.3: Particle size distribution of substrates. Each value represents a mean of two replicates.

Substrate	(% w/w)				
	0.0 - 2.8 mm	2.9 - 4.0 mm	4.1 - 6.7 mm	6.8 - 12.6 mm	>12.70 mm
Bauxite	0.2	0.0	2.6	75.7	21.5
Shale	1.9	5.3	25.6	41.9	25.3
BOS	22.3	11.8	21.9	22.6	21.4
Limestone	1.2	2.2	8.6	26.3	61.7
Zeolite	0.0	0.0	4.2	83.6	12.2
LECA	0.4	0.1	4.3	25.0	70.2
Fly ash	77.8	3.5	6.5	12.2	0.0

2.3.2. Phosphorus adsorption characteristics

Fly ash and shale showed the best P adsorption characteristics, followed by bauxite, limestone, and LECA (Figure 2.1). When P adsorption data were plotted according to the Langmuir model of adsorption (Figure 2.2), a close fit ($p < 0.05$) to equation (2) was observed for all the substrates, with the exception of zeolite. Therefore, theoretical P adsorption maxima b and bonding capacities a of the substrates were determined and are shown together with the correlation coefficients r and regression lines y in Table 2.4.

Theoretical (obtained from the Langmuir equation (2), Table 2.4) and empirical (from Figure 2.1) maximum P adsorption values were plotted against each of the investigated physical and chemical properties of the substrates (pH, CEC, hydraulic conductivity, porosity, surface area and bonding capacity). In the former case (theoretical P values), porosity was the only significant factor ($r^2 = 0.71$; $p < 0.05$) (Table 2.5). When empirical maximum P adsorption values were plotted against the physical and chemical properties, hydraulic conductivity became the most significant parameter ($r^2 = 0.71$; $p < 0.05$) (Table 2.5). In general, the physical and chemical properties listed in Table 2.2 were not strongly linked with the observed P adsorption

capacities.

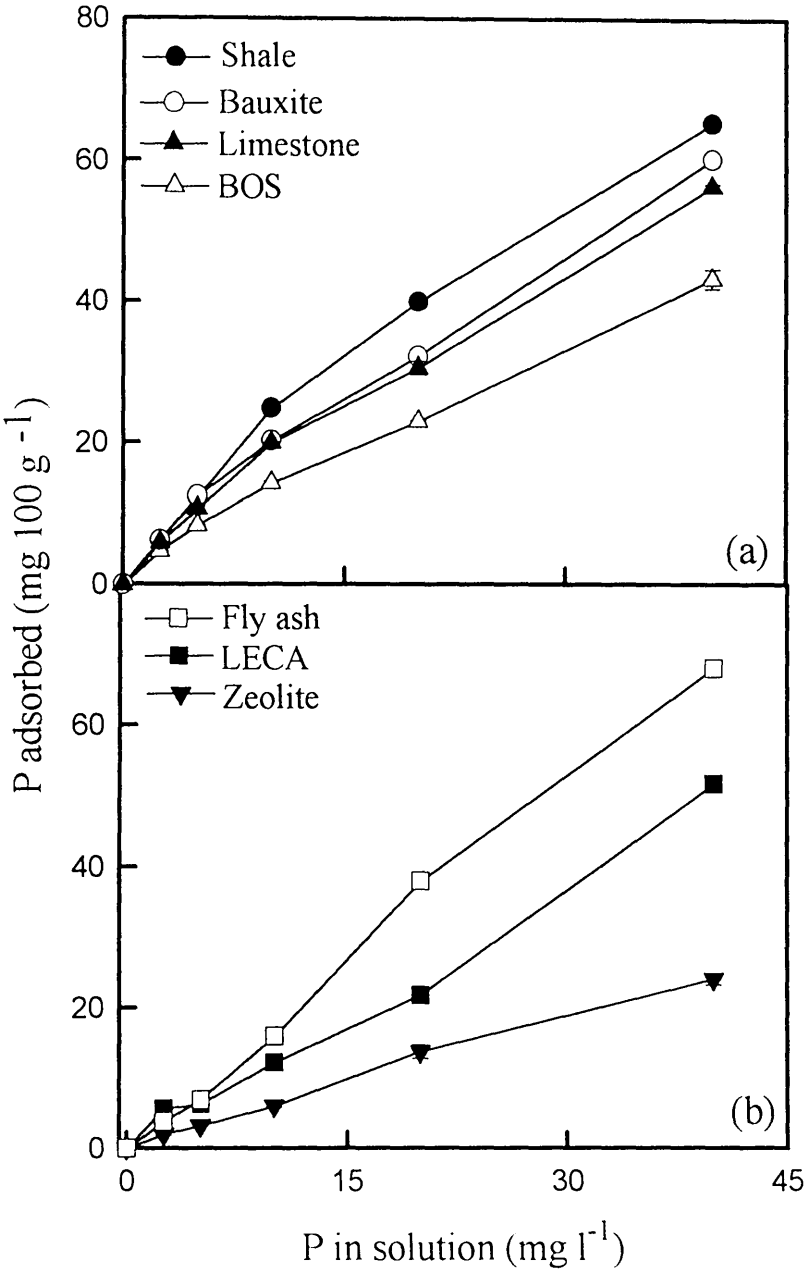


Figure 2.1: P adsorption isotherms for seven different substrates. Each point represents a mean value of three replicates. Vertical bars denote standard deviation (SD). Solutions equilibrated for 24 h at constant temperature (21°C).

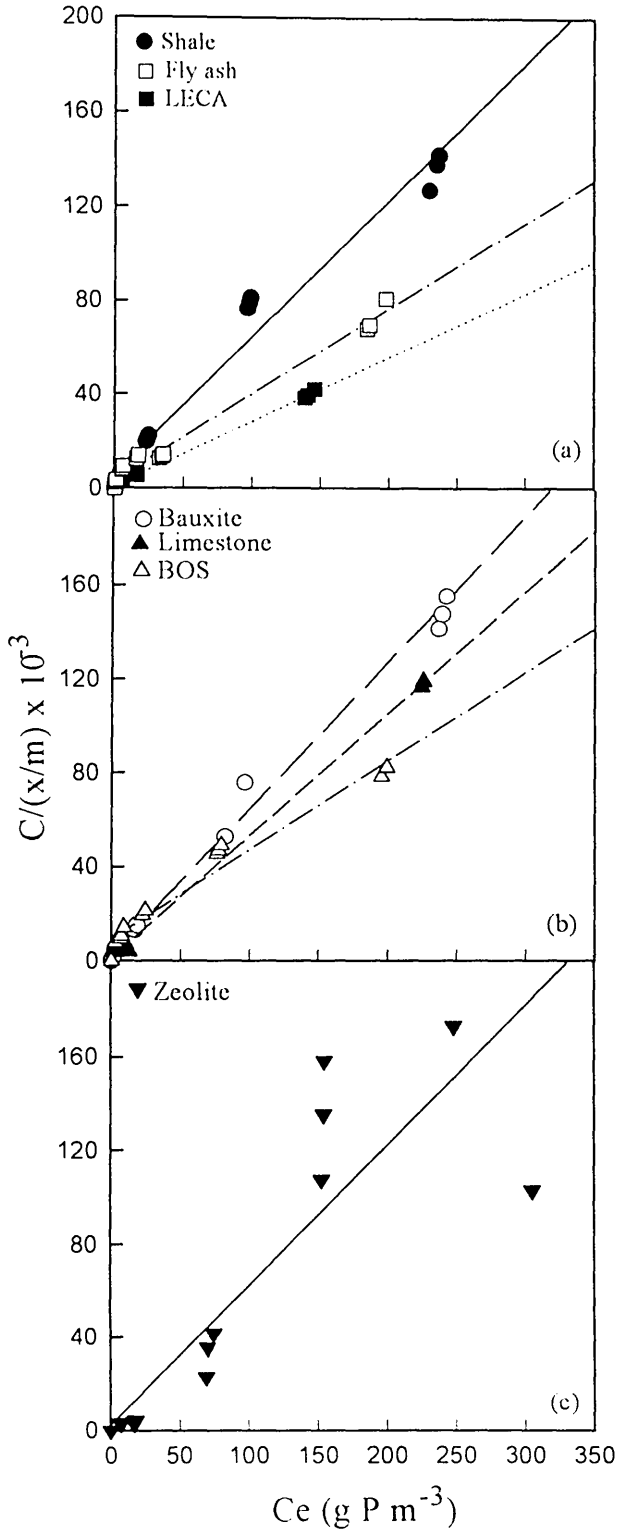


Figure 2.2: Langmuir plot of P adsorption data for all seven substrates.

Table 2.4: Theoretical P adsorption maxima, bonding capacities *a*, correlation coefficients *r*, and regression line *y*.

Substrate	P adsorption max (g kg^{-1})	*a*	*r*	*y*
Bauxite	0.59 ± 0.03	0.49	0.991	0.62 x + 2.70
Shale	0.65 ± 0.07	1.73	0.974	0.58 x + 6.34
BOS	0.56 ± 0.02	0.09	0.968	0.38 x + 9.48
Limestone	0.64 ± 0.02	0.25	0.998	0.52 x + 1.30
Zeolite	1.00 ± 0.08	0.01	0.810	0.60 x + 2.26
LECA	0.84 ± 0.05	0.04	0.998	0.27 x + 1.11
Fly ash	0.95 ± 0.01	0.36	0.988	0.36 x + 3.70

The four substrates chosen for further analysis were shale, bauxite, fly ash and LECA, which included both the materials with the highest P adsorption capacities, and also represented a wide range in pH.

After 40 days of exposure of these substrates to the extremely high P loading rates of the synthetic waste water solution (25 g P m^{-3} d^{-1}), saturation had not been reached (Figure 2.3 a). Shale adsorbed the highest amount of P (400 mg P kg^{-1}), followed by fly ash (300 mg P kg^{-1}), and then bauxite (160 mg P kg^{-1}). However, as fly ash had already been used because of its high P adsorption capacities in investigations carried out by other authors (Theis and McCabe, 1978; Mann and Bavor, 1993), it was decided to continue the investigation using only the shale and bauxite.

To speed up the saturation of the substrates, the P concentration of the feeding solution (42 mg l^{-1}) and the daily flow through the system (3 l d^{-1}) were doubled, thus increasing the inlet loading rate 4 -fold (from 25 to 100 g P m^{-3} d^{-1}). This resulted in a sharp rise in the rate of P adsorption for the following 20 days, which reached saturation at times between 65 and 80 days (Figure 2.3 b). Overall, the total input of P to the substrates over the whole period of investigation was 24.7 g, the total output P of shale was 21.8 g and the total adsorbed 2.9 g, giving a saturation presented in Figure 2.3 a, b. value of 0.73 g P kg^{-1} of shale. Cumulative P adsorption

capacities of substrates are presented in Figure 2.3a,b.

Table 2.5: Regression analysis of P adsorption capacity against measured physical and chemical parameters

Parameter	r^2	
	Theoretical (Langmuir)	Empirical
Hydraulic conductivity	0.21_{ns}	0.71^{*}
Porosity	0.71^{*}	0.39_{ns}
pH	0.11_{ns}	0.01_{ns}
CEC	0.04_{ns}	0.33_{ns}
Specific surface area	0.32_{ns}	0.32_{ns}
Bonding capacity **a**	0.10_{ns}	0.32_{ns}
Fe content	0.35_{ns}	0.30_{ns}
Al content	0.07_{ns}	0.09_{ns}

* significant ($p < 0.05$); ns - non significant n = 7

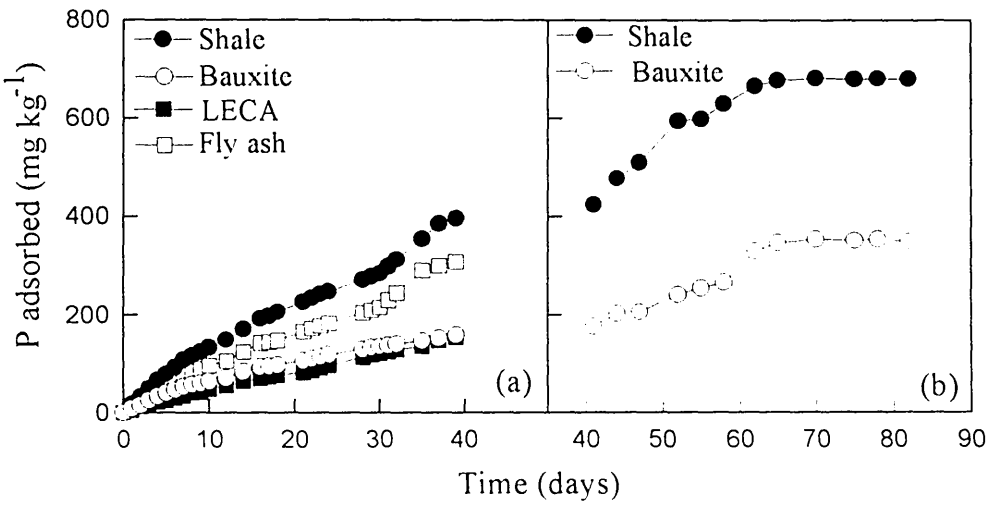


Figure 2.3: Cumulative P adsorption capacities for (a) shale, bauxite, LECA and ash over 40 days and (b) shale and bauxite only for the following 40 days. The columns were fed from below with the synthetic sewage solution containing 35 - 42 mg P l^{-1} (as KH_2PO_4) during the first 40 days of experimentation, followed by 70 - 90 mg P l^{-1} (40 days) from a common reservoir, using a separate peristaltic pump for each column.

2.3.3. X-ray fluorescence analysis

After the saturation point of P had been reached, subsamples of the substrates from each tube were examined; changes in colour were observed on the surfaces of both bauxite and shale, suggestive of precipitation of insoluble phosphates. The bauxite had dark patches, and the shale orange ones. Investigation of the coatings by XRF showed that P deposition had occurred only on the shale particles; the concentration of P increased roughly 3-fold during the period of exposure in the column, as indicated by the X - ray count rate (Figure 2.4), which is directly proportional to the P concentration (Brindley and Brown, 1980). However, the nature of the dark patches on bauxite was not discovered.

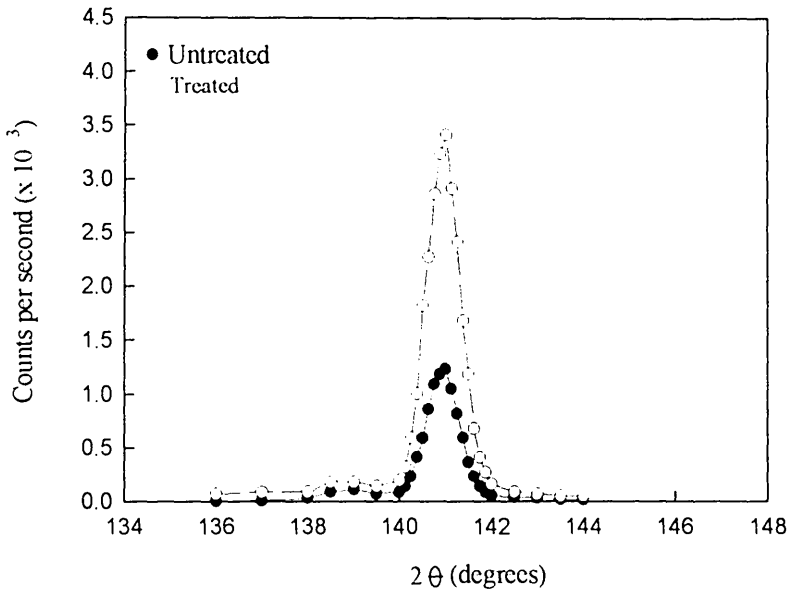


Figure 2.4: XRF peaks due to phosphorus, untreated and treated shale samples.

2.3.4. Suitability of substrates for plant growth

The visible characteristics of the plants grown in the different substrates are summarised in Table 2.6. Growth was generally similar in all four substrates, but there were some variations. Red marks observed on plant stems indicating possible P

deficiency (Blackmoore and Tootill, 1984) were most obvious in bauxite and shale substrates, while the development of young shoots was most prominent in shale. However, elemental analyses of the plant material grown in different substrates did not show any significant difference in the mineral content of the plants.

Table 2.6: Plant growth in different substrates

Substrate	Plant growth
Shale	Very good, although red marks observed on stems after two weeks indicating deficiency in P. Good development of young shoots.
Bauxite	Good: as in shale, red marks observed on stems.
LECA	Very good: however, development of young shoots not so obvious as in shale substrate.
Fly ash	Fairly good: after three weeks slight yellowing observed on the edges of the leaves.

2.4 Discussion

P adsorption appears to be mainly a surface phenomenon, and occurs most readily on such surfaces as those of iron and aluminium oxides and hydrous oxides (Ryden and Pratt, 1980; Stuanes, 1984). These have an external layer of OH^- ions and water molecules, which are coordinated with Fe^{3+} or Al^{3+} ions directly below the surface. In the ideal structure the surface is assumed to have no net charge, and therefore at a freshly cleaved surface OH^- ions and water molecules can replace the structural O_2- and OH^- ions, which become exposed (Parfitt, 1978). It is well known that materials rich in Fe and Al may have an affinity for P as phosphate displaces water or hydroxyls from the surface of Fe and Al hydrous oxides (ligand exchange reactions) to form monodentate and binuclear complexes within the coordination sphere of the hydrous oxide (Bache and Williams, 1971; Parfitt et al., 1975; Mott, 1981; Richardson, 1985).

In acid environments, inorganic P is adsorbed on hydrous oxides of Fe and Al and may precipitate as insoluble Fe phosphates (Fe-P) and Al phosphates (Al-P). In alkaline environments, precipitation as insoluble Ca phosphates (Ca-P) takes place at pHs greater than 7 (Richardson and Craft, 1993).

Although negative correlation between phosphate adsorption and pH is found in minerals, it has been difficult to establish the relationship between these two properties in most of the reported experiments, mainly due to the difficulties in finding minerals which differ only in pH (Stuanes, 1984). Therefore it is not surprising that there was no relationship between the pH values of the materials used in the present work and their P adsorption capacities (Table 2.5).

The relationship between cation exchange capacity and P adsorption was difficult to establish, because the strength of bonding of cations by the exchange sites depends on different parameters such as the nature of the source of the negative charge, hydration status and valency and size of each cation (Barber, 1984). The relationship between cation exchange capacity and P adsorption was not significant. This is not surprising, as there is no obvious mechanism by which this property is likely to affect the adsorption of anionic species.

The measured hydraulic conductivities of 2 - 29 x 10^{-4} m s^{-1} (Table 2.2) were in the range of values recommended for CWS (EC/EWPCA, 1990), and it has been suggested that once developed, hydraulic conductivity will stabilize and maintain itself (Kickuth, 1977). Much lower values have been measured in studies in Denmark, Austria and UK (Schierup et al., 1990). Brix (1994) pointed out that the hydraulic conductivity often decreases and usually stabilizes in the range of 10^{-5} to 10^{-6} m s^{-1} and that therefore the dimensions of constructed wetlands with subsurface flow should not be based on the assumption that the hydraulic conductivity will increase as a consequence of root and rhizome growth. Recent results presented by Sanford et al. (1995) support this statement, as the hydraulic conductivity of investigated substrates (pea gravel and coarse gravel) did decrease in the 26-month period of their study.

Porosity and hydraulic conductivity had the most significant influence on P adsorption capacities of the materials (Table 2.5). The apparent relationship between porosity and P adsorption has no obvious interpretation. One might expect that porosity had a role because it was associated with surface area, but the direct comparison of this latter variable showed no relationship. No mechanism can be suggested, either, for the apparent relationship with hydraulic conductivity. Thus the correlations indicated by Table 2.5. must be treated cautiously.

The material with the smallest particle size distribution will have the highest surface area, increasing the potential for direct reaction with phosphates. The measurements showed such a trend for most of the substrates investigated, but zeolite was an exception; it had the highest specific surface area (Table 2.2) and the highest theoretical P adsorption capacity (Table 2.4) but the lowest amount of P adsorbed per 100 g of material (Figure 2.1). The reasons for this may be, firstly, that P adsorption equilibration is limited by diffusion, so that larger particles (84 % of zeolite particles were between 6.8 and 12.6 mm (Table 2.3)) absorb less than 10 % of P from the solution (Crank, 1975, Fig 6.4., p 95); and secondly, the Langmuir equation may be inappropriate in this context. There is a considerable controversy over the proper use of the Langmuir equation for adsorption studies, arising from the fact that it was developed from the assumption that adsorption of gases forms a monomolecular film on uniform surfaces, whereas the adsorption of phosphate on minerals involves adsorption onto non-uniform surfaces (Barrow, 1978; Barber, 1984). The biggest advantage in the application of the Langmuir model for adsorption studies is that it enables the calculations of theoretical P adsorption maxima to be made. Therefore, despite the limitations of the mechanistic P adsorption equations, they are still widespread in P adsorption studies, with Langmuir equations being most frequently used (Stuanes, 1982). However, where there is a lack of close fit to the Langmuir equation as in the case of zeolite in this study (Figure 2.2), the results should be treated cautiously because extrapolations to determine maximum adsorption may be inaccurate (Barber, 1984).

Of the seven investigated substrates, fly ash, shale and bauxite were chosen for further

examination of the P saturation point based on their high P adsorption and bonding capacities (Table 2.3). In addition, LECA was studied despite its low bonding capacity value, because experiences in Scandinavian countries suggested that it was a new and promising substrate (Brix, 1994).

The results of the P saturation point measurements (Figure 2.3) indicated that shale has the highest P adsorption capacity, in excess of 650 - 700 mg kg^{-1}. The closest reported values for the materials used in CWS are 430 mg P kg^{-1} for blast furnace slag and 240 mg P kg^{-1} for fly ash (Mann and Bavor, 1993). Zhu *et al* (1997) recently showed that some types of Norwegian lightweight expanded aggregates (LWA) have P adsorption capacity of 1390 mg P kg^{-1}. On the other hand, Johansson *et al.* (1997) concluded that Swedish produced LWA was chemically non-reactive and therefore was not suitable for P removal unless lime was added. As the production of LWA requires substantial amounts of energy, the overall suitability and cost effectiveness of this material as a substrate for a CWS remains to be explored.

The presence of P deposition on shale surfaces during exposure to the synthetic waste water solution was confirmed by X-ray fluorescence analysis, indicating the occurrence of precipitation reactions (Figure 2.4). Such precipitation may lead to enhanced removal of P. This has particular implications for wastewater treatment; Stuanes (1984) showed that P removal by soils receiving long-term wastewater treatment applications was much greater than that predicted by adsorption maxima. One suggested explanation is the rejuvenation of exchange sites by precipitation during alternating oxidizing and reducing soil conditions (Faulkner and Richardson, 1989).

2.5. Conclusions

The results of this chapter consistently suggest shale as a substrate with a large potential for P removal, with the P adsorption capacity as high as 0.65 - 0.70 g kg^{-1}.

Shale was also a good growth medium for *Phragmites australis*, with good development of rhizomes and young shoots. In addition, XRF analysis of the shale surface (after being exposed to high P concentration for a period of 80 days) indicated P removal via precipitation on the material.

The physical and chemical properties listed in Table 2.2 were not strongly linked with the observed P adsorption capacity, and the differences between materials are better explored by direct observations of P adsorption in laboratory experiments.

Chapter 3: The performance of a greenhouse (pilot scale) constructed wetland for phosphate and ammonium removal from waste water[2]

3.1. Introduction

After extensive laboratory investigations of the possible substrates for a constructed wetland system described in the previous chapter, the next stage was to build a system in a greenhouse and assess its performance with regard to both phosphate and ammonium removal from wastewater. This is very important from the practical point of view as it provides the information on the efficiency of the chosen substrate. In addition, a small scale system enables detailed investigation of internal nutrient removal processes to be made, as different components are more easily isolated and manipulated (Cooper and Findlater, 1990; Moshiri, 1993).

With respect to assessing the performance of a constructed wetland, there are two measures in common use. One of them, concentration treatment efficiency, expressed as a percentage of a pollutant removed by the wetland based on inlet and outlet concentrations has been used for over a decade (Stark and Williams, 1995). However, this method of interpreting the results does not provide information about the quantity of pollutant removed per unit time, or the actual size of the system (Hedin and Nairn, 1990; Tchobalogonous, 1996). In order to overcome this problem, a new way of measuring was introduced, where loading rates (concentrations times flow) were divided by the plan surface area of the system giving an area adjusted unit of removal

[2] This chapter is based on a paper entitled 'Phosphate and ammonium removal by constructed wetlands with horizontal subsurface flow, using shale as a substrate', published in *Water Science and Technology* 35, Vol 5, 1997.

expressed as g pollutant m^{-2} day^{-1}. The main advantage in the use of this kind of measurement is that it takes into account concentration, flow and wetland area and therefore provides a better insight into wetland treatment performance (Brix, 1994a; Tchobalogonous, 1996).

The present chapter describes:

i) simultaneous phosphate (P) and ammonium (N) removal from synthetic sewage in a greenhouse CWS, over a period of 11 months;

ii) the contribution of *Phragmites australis* to P and N removal from waste water, by estimating O_2 release from plant roots; comparing P and N removal rates in planted and unplanted tanks and calculating the nutrient uptake by the above - ground biomass.

3.2. Methods

3.2.1. Performance of the greenhouse tanks

The CWS was housed within an unheated greenhouse without artificial lighting. Seedlings of *Phragmites australis* were grown from rhizome transplants in a nursery bed of shale until they reached an average height of 0.6 m (4 weeks). Shale was obtained from the same quarry (Cultshill, Ladybank) as the one used for the laboratory experiments (Chapter 2). Eight 250 l water tanks (1.0 m long, 0.50 m deep and 0.50 m wide) were each filled with 200 kg of shale. The volume of the material in each tank was 165 l with a pore space of approximately 50 l. Four were planted with seedlings (T2, T8, T4 and T6) and four left unplanted as controls (T1, T7, T3 and T5). They were left to grow for three months before wastewater was applied. Each tank was connected to a reservoir containing 250 l of synthetic sewage, via a

peristaltic pump, to distribute the wastewater through the wetland (Figure 3.1).

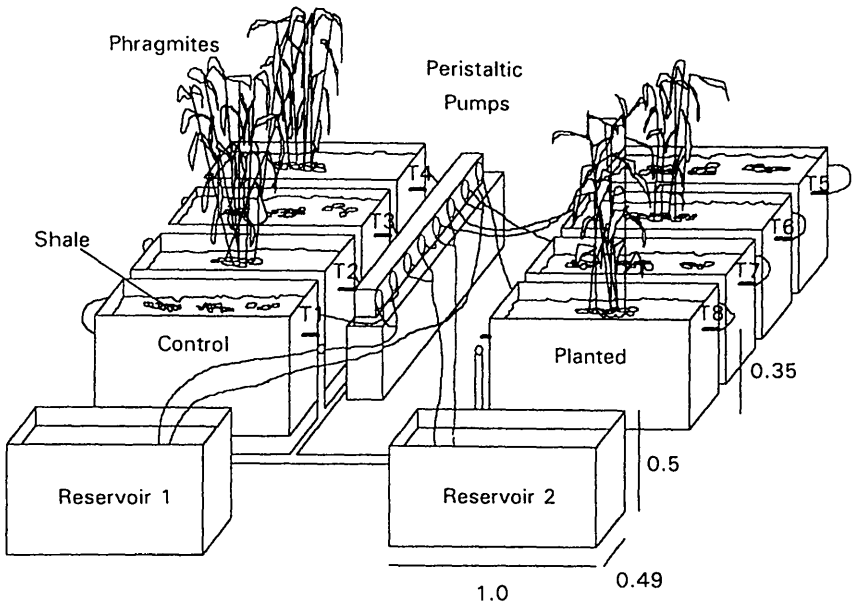


Figure 3.1: The greenhouse set - up showing arrangement of tanks and reservoirs, and their dimensions (m). Only a few plants are shown.

The pump was set to operate 4 times each day for 50 minutes, at a rate of 3 l h^{-1}. With this arrangement, 10 l day^{-1} of waste water passed through the system, giving a residence time of 5 days. The surface area of each tank was 0.5 m^2. Real sewage was used only during the first 10 days at the beginning of the experimental period, in order to establish a microbial community similar to the real CWS systems. This decision was made because it was not possible to connect reservoirs to the sewage supply anywhere in the area. The alternative would have been to bring the very large volumes of sewage necessary for the experiment (500 l) which would have had to be brought manually from the Dunfermline sewage works (40 km distance) once a week. Therefore, the investigation continued using a synthetic sewage devised by DoE (1981), which was prepared every 5 days. The synthetic sewage (made up by mixing 7 different components: bacteriological peptone, meat extract, urea, sodium chloride, calcium chloride, magnesium sulphate and dipotassium hydrogen phosphate) is widely

used as a substitute for real sewage in the Water Research Council's waste water treatment studies in Great Britain (Appendix 1)

Plate 3.1: The greenhouse set-up showing arrangement of tanks and reservoirs after 10 months from the establishment of a CWS

Such synthetic sewage after dilution contains approximately 106 mg l^{-1} organic C, 46 mg l^{-1} N and 5 mg l^{-1} P (DoE, 1981). In order to investigate the capacity of the systems for phosphate and ammonium removal over a wider range of nutrient input concentrations, the contents of N and P in a synthetic sewage were modified. While N

content was decreased 2 - 4 times (by decreasing the concentrations of bacteriological peptone and urea), P content was increased 2 - 8 times (by increasing the concentrations of dipotassium hydrogen phosphate, Appendix 1). This kind of modification resulted in a very unusual N/P ratio of the synthetic sewage (approximately 0.6 :1) when compared to the real one (approximately 2:1) which might have had an influence on the experimental results as well as the mass balance observations. However, the contents of the synthetic sewage had to be modified in this way, because one of the aims of the experiment was to achieve substrate saturation by P, which meant that the P concentration had to be reasonably high, and secondly, N concentrations had to be decreased because of the upper limit of the concentration range of the automatic N analysis system (there were too many samples to be analysed to permit large numbers of repeated analyses at different dilutions). Therefore, the tanks were fed from two separate reservoirs. Four of them (T1, T7, T2 and T8) were fed with average inlet concentrations of 8 - 12 g NH_4^+ m^{-3} (0.16 - 0.24 g m^{-2} day^{-1}), 0.1 - 0.2 g NO_3^- m^{-3} (0.002 - 0.004 g m^{-2} day^{-1}) and 10 - 20 g $H_2PO_4^-$ m^{-3} (0.2 - 0.4 g m^{-2} day^{-1}), while the remaining four (T3, T5, T4 and T6) were fed with double these concentrations throughout the whole period of investigation. However, the synthetic sewage concentration in terms of BOD was kept the same in all tanks (Elloriaga, 1996).

After 10 months, the inlet phosphate concentration in tanks T3,T5, T4 and T6 was increased to 120 g m^{-3} with the aim of reaching saturation. The nutrient concentrations in the synthetic sewage, at the inlets and outlets of the tanks, were monitored every 5 days at the early stages of the experiment, and then once a week. $H_2PO_4^-$ was determined using the standard ammonium molybdate method (DoE, 1980). NH_4^+ was measured using the method by Crooke and Simpson (1971) and NO_3^- by the method described by Best (1976) using a Chemlab Instruments Ltd

continuous flow analyser. Additional samples were taken for measurements of pH, redox potential (E_h) and temperature (t) in order to investigate the possible effects of these parameters on P and N removal from waste water. pH and E_h values were measured by standard techniques described by Rowell (1994), using a conventional glass electrode, a calomel reference electrode and a platinum electrode. However, E_h readings were not corrected for pH nor was a 248 mV addition used to correct for the zero potential of the platinum electrode. Temperature was measured using a combined oxygen electrode and temperature recorder.

3.2.2. Contribution of *Phragmites australis* to phosphate and ammonium removal

The nutrient removal of the planted and unplanted tanks was monitored for 11 months. In January 1996, the above-ground biomass of the plants was harvested and the fresh weights recorded. The height of the plants was approximately 1.2 m and the fresh weights were 1022, 909, 1400 and 942 g for T2, T8, T4 and T6 respectively. Plant material was then oven dried at 100 ^{o}C overnight and weighed to determine the dry matter content (DM). Concentrations of mineral elements were determined after digestion (Rowell, 1994) using an inductively coupled argon plasma spectrometer (ICP) (DoE, 1986).

The amount of O_2 which may be present in the substrate is important because anaerobic conditions may reduce P adsorption and prevent any conversion of ammonium to nitrate. Therefore a separate experiment was conducted in order to estimate O_2 release from plant roots. Twelve rectangular pots (0.61 m long, 0.17 m deep and 0.17 m wide) were filled with 9 kg of shale and divided into three groups of four pots to give three replicates. For each replicate, two pots were planted with the

Phragmites australis seedlings and two kept as controls (Plate 3.2). Each of the planted pots contained between 26 and 30 new green stems (approximately 15 to 30 cm high), 5 to 8 young shoots (height < 5 cm) and 70-80 dead culms. In addition, one each of the planted and unplanted pots sealed with a layer of paraffin (1 cm thick) in order to prevent atmospheric O_2 entering the system. The volume of the material in each pot was approximately 0.0145 m^3 with a pore space of approximately 0.0035 m^3. Each pot was connected to a peristaltic pump, set to operate 4 times each day for 3.5 minutes, giving a retention time of 5 days. Dissolved O_2 concentrations in the wastewater were measured in samples daily at the beginning of the experiment, and then taken at the inlet and outlet every fifth day, using the dissolved oxygen meter (Jenway 9071, UK). Comparison between sealed and non-sealed water pots was made.

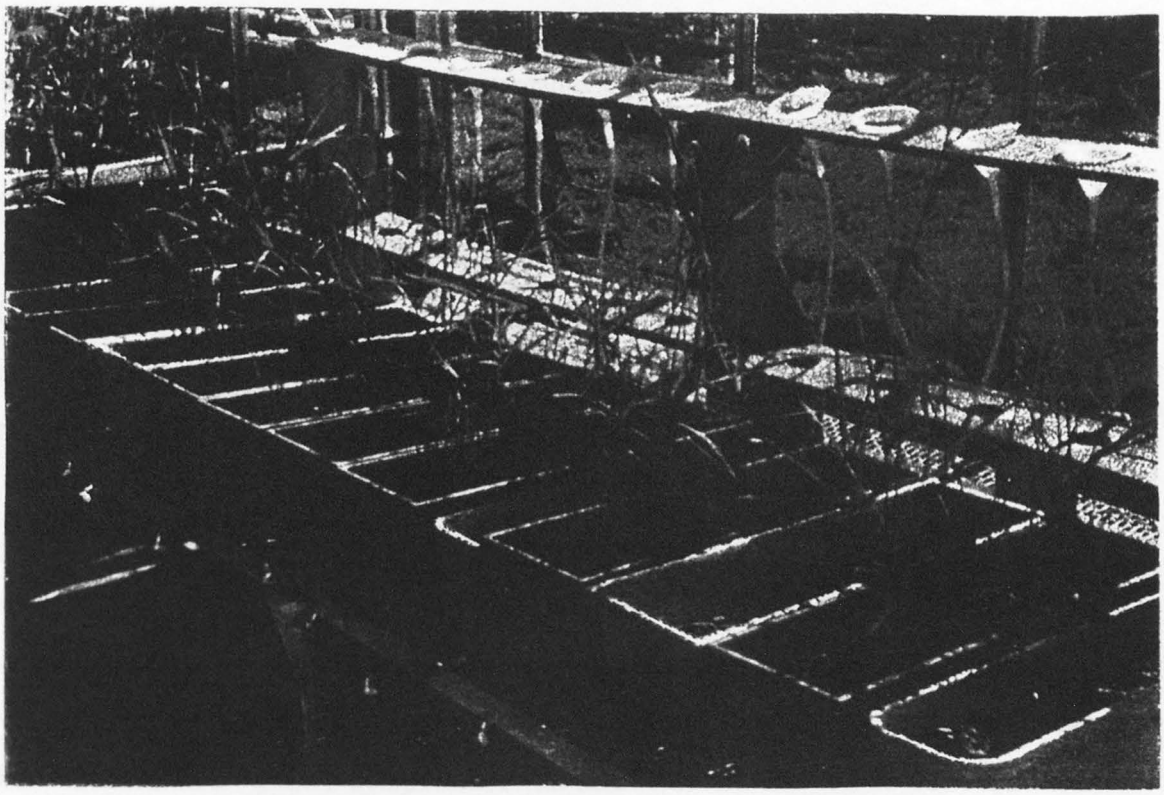


Plate 3.2: Arrangement of rectangular pots, used to estimate O_2 release from plant roots.

3.3. Results

3.3.1. Performance of the greenhouse tanks

Long term phosphate, ammonium and nitrate loading rates (plan surface area) and corresponding percentage removal rates are presented in Figures 3.2, 3.3 and 3.4, respectively. The total input of P over the whole period of investigation (309 days) was 348.8 g P m^{-2}, while the total output in the unplanted and planted tanks was 10.8 g P m^{-2} and 1.6 g P m^{-2}, respectively. Virtually complete removal of phosphate (P) was achieved over the whole period of investigation even when the influent concentration rates were increased to 120 g m^{-3} (2.4 g m^{-2} day^{-1}, Figure 3.2 b) on the last two sampling occasions, for both planted and control tanks.

The total input of mineral N (NH_4^+ + NO_3^-) over the whole period of investigation was 162.1 g N m^{-2}, and the total output 71.2 g N m^{-2} (unplanted tanks) and 1.4 g N m^{-2} (planted tanks), respectively. Ammonium was completely removed in the planted tanks, while in the control tanks it varied between 40 and 75 %, suggesting that the contribution of the plants was substantial, between 25 and 60 % (Figure 3.3). Nitrate concentrations in planted tanks fell from 0.2 - 0.4 g NO_3^- m^{-3} to 0.02 g NO_3^- m^{-3} (with the exception of days 50 and 230) while in unplanted tanks outlet concentrations fell to approximately 0.05 - 0.08 g NO_3^- m^{-3} ; however, it should be noted that influent nitrate levels were extremely low (Figure 3.4).

pH, E_h and temperature values are presented in Figure 3.5. pH values of the influent ranged from 6.5 to 7.5, with the effluent values between 4 (on a first sampling occasion) and 6.5, being fairly stable throughout the whole period of investigation. Eh values of the influent ranged from -30 to 30 mV, while the values of the effluent were between 170 and 50 mV. Temperature values of the effluent ranged between 20 and 10 ^oC, during summer and autumn, falling to 5 ^oC in winter (in January of 1996 the outside temperature values decreased to below 0 ^oC).

No significant correlation was found between $H_2PO_4^-$ - P removal rates (%) and the pH, Eh and t (Figure 3.6) or between NH4+- N removal rates (%) and the pH, Eh and t (Figure 3.7) over the period of investigation at both low and high phosphate and ammonium input loading rates. Also, forward stepwise regression analysis showed that the combined effect of any of these three variables did not significantly affect P or N reduction.

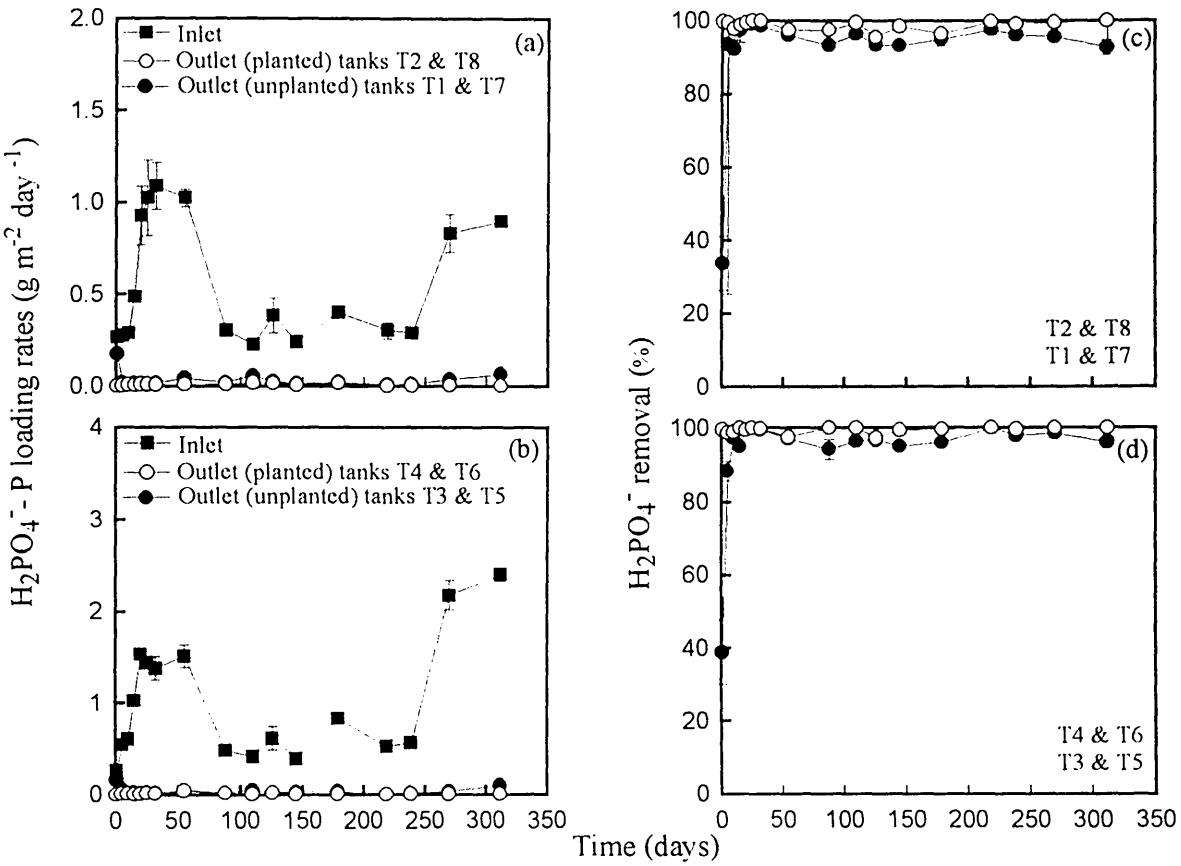


Figure 3.2: $H_2PO_4^-$ - P removal for the period from 23/07/1995 - 20/05/1996. In (c) and (d) open symbols represent removal of phosphate in planted tanks, solid symbols removal in unplanted. Vertical bars denote standard deviation (sd).

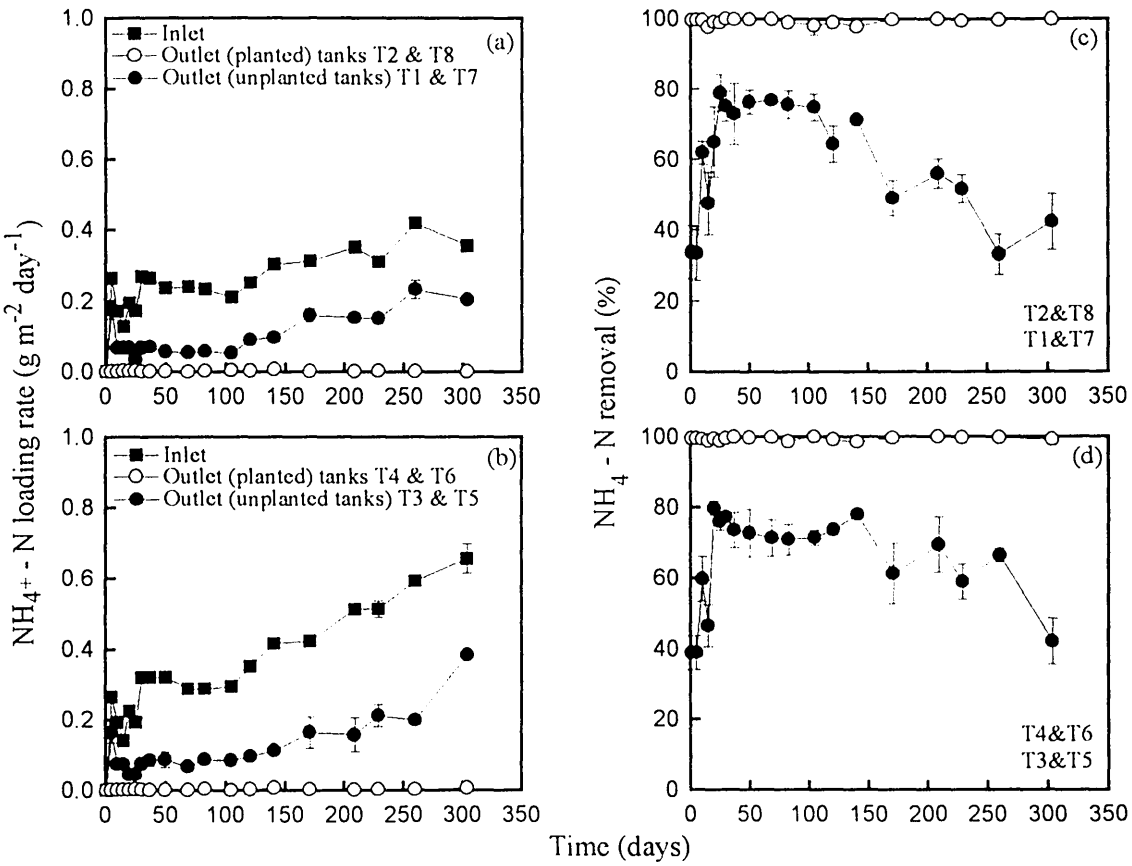


Figure 3.3: NH_4+ - N removal for the period from 23/07/1995 - 20/05/1996. In (c) and (d) open symbols represent removal of ammonium in planted tanks, solid symbols removal in unplanted. Vertical bars denote standard deviation (sd).

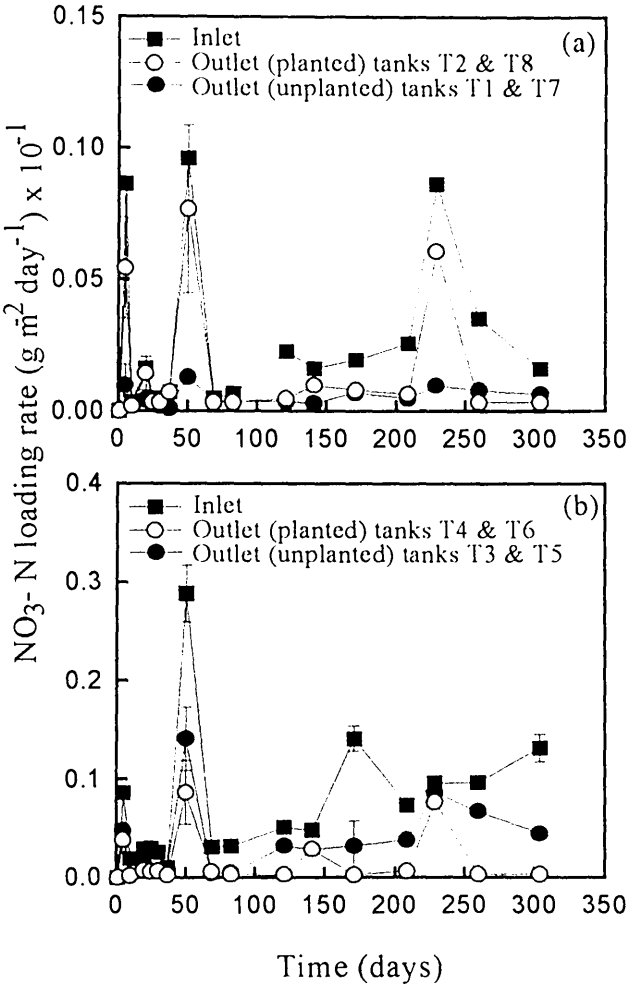


Figure 3.4: NO_3^- - N removal for the period from 23/07/1995 - 20/05/1996. Each value represents a mean of two replicates. Vertical bars denote standard deviation (sd).

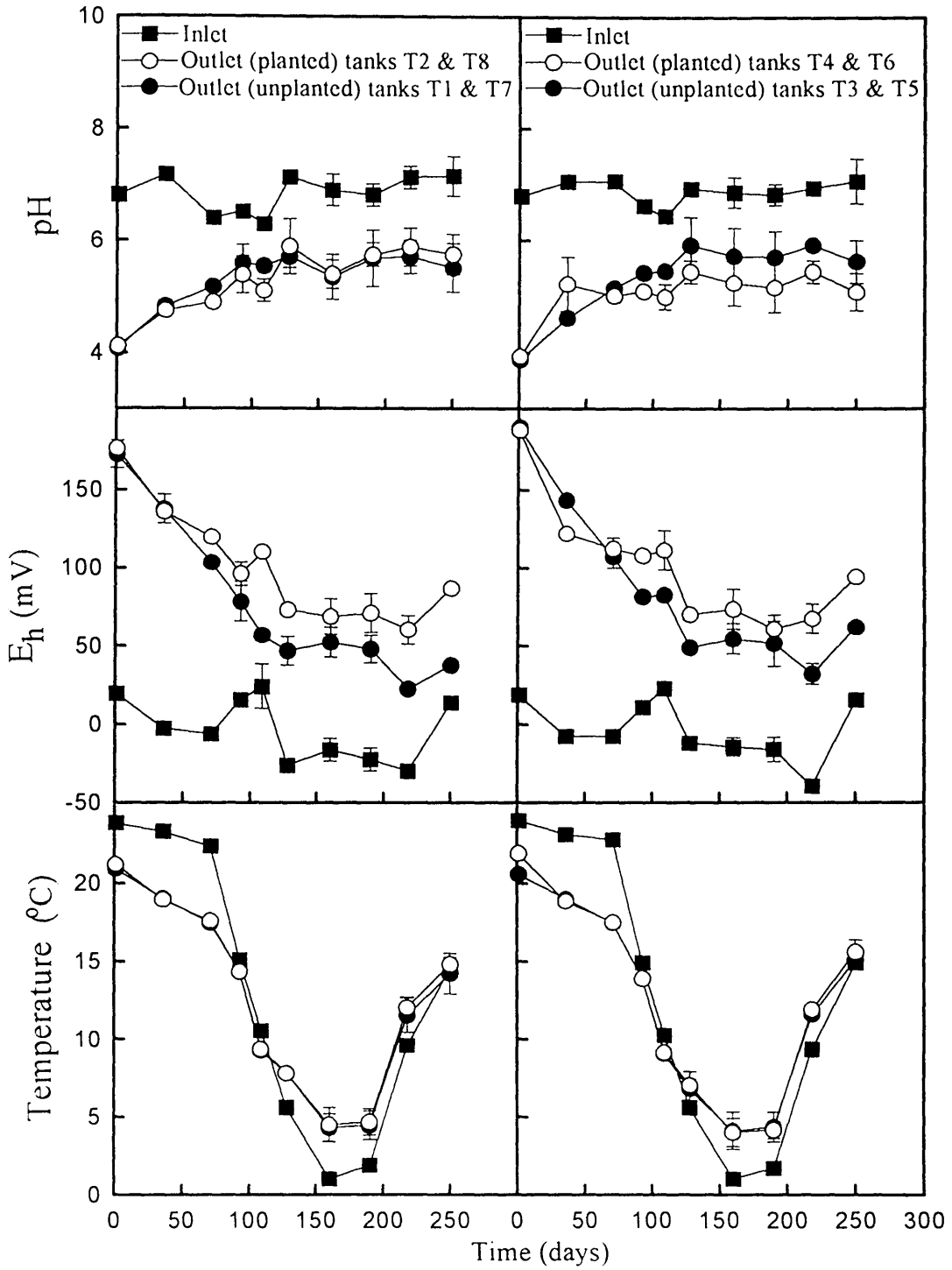


Figure 3.5: pH, E_h and temperature values for the period from 02/08/1995 - 06/04/1996. Each value represents a mean of two replicates. Vertical bars denote standard deviation (sd).

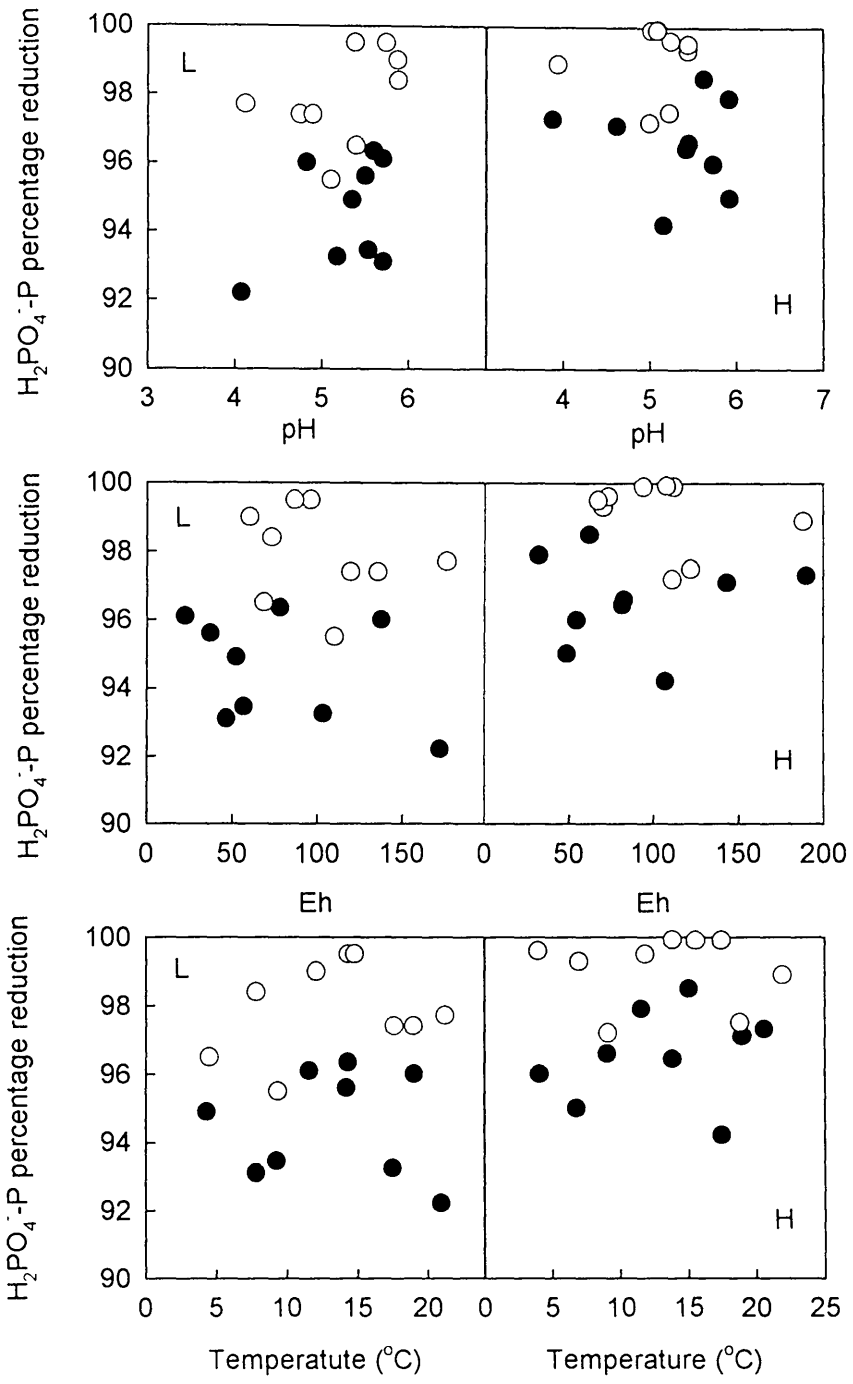


Figure 3.6 - Values of $H_2PO_4^-$-P percentage reduction plotted against values of pH, Eh and temperature (at the outlets) in the planted (○) and unplanted (●) tanks at low (L: 10 - 20 g m^{-3}; 0.2 - 0.4 g m^{-2} day^{-1}) and high (H: 20 - 40 g m^{-3}; 0.4 - 0.8 g m^{-2} day^{-1}) P loading rates.

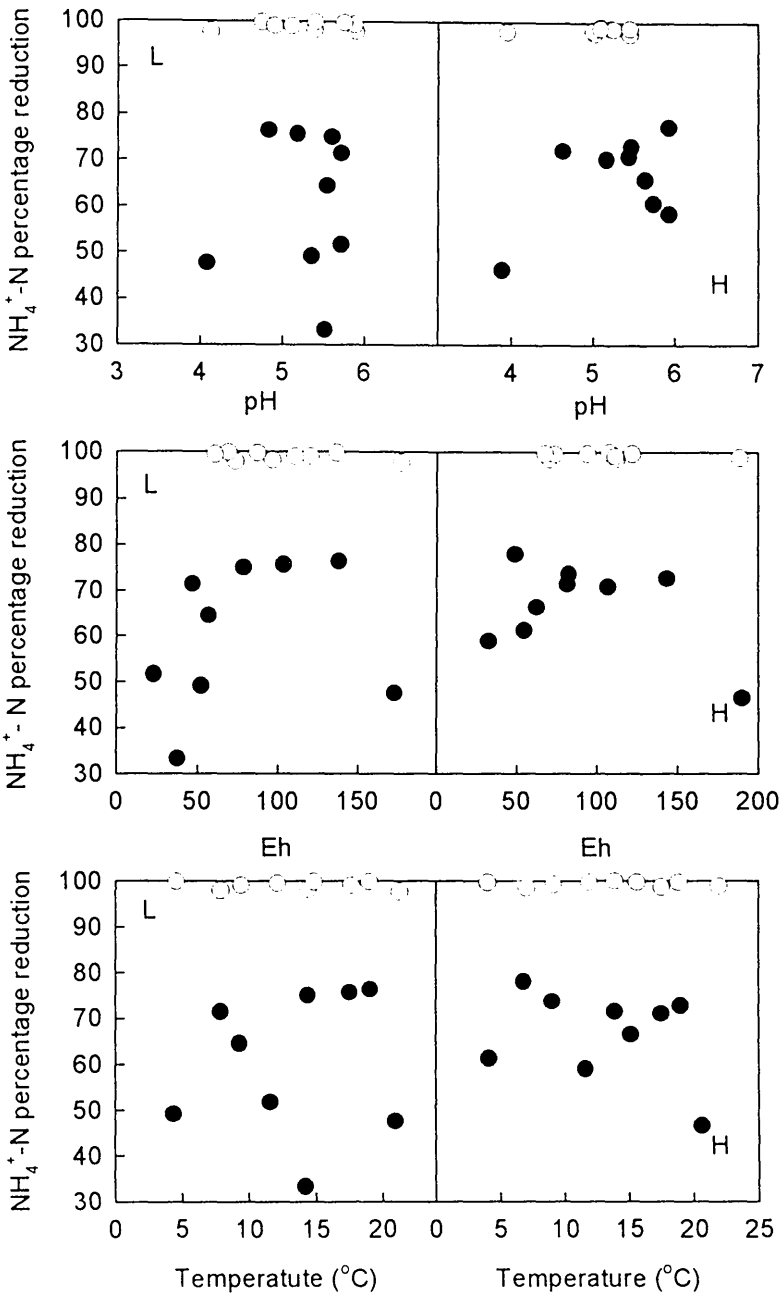


Figure 3.7 - Values of NH_4^+ - N percentage reduction plotted against values of pH, Eh and temperature (at the outlets) in the planted ( ) and unplanted (●) tanks at low (L: 8 - 12 g m^{-3}; 0.16 - 0.24 g m^{-2} day^{-1}) and high (H: 16 - 24 g m^{-3}; 0.32 - 0.48 g m^{-2} day^{-1}) N loading rates.

3.3.2. Contribution of *Phragmites australis* to phosphate and ammonium removal

3.3.2.1. Nutrient removal in planted versus unplanted tanks

In order to test the effects of the presence of plants and different inlet concentrations on P and N removal, pH, E_h and temperature, four two-way ANOVA analyses were performed (one test for each season), using Sigma Stat statistical software (Kuo *et al.*, 1992). Each of the treatments had two replicates and tests were performed on absolute values (Table 3.1).

The presence of *Phragmites australis* in planted tanks had a significant effect on the changes in $H_2PO_4^-$- P, NH_4^+ - N and NO_3^- - N removal rates in all four seasons whereas different (high/low) concentrations only had a significant effect on NO_3^- - N in each season (Table 3.1). It was only in the final period of investigation, the following spring, that the effect of inlet concentration on $H_2PO_4^-$- P and NH_4^+ - N became apparent. In summer, the inlet concentration had an effect on the changes in both pH and E_h , while in spring it had an effect only on E_h. Temperature was affected only by the presence of plants on two occasions, in summer and spring (Table 3.1).

Elemental analysis of the plants prior to planting, after 3 months growing in shale and after 5 months of the waste water application, showed almost no difference in P and N concentrations (Table 3.2). However, Fe, Mn and Zn concentrations varied considerably ($p < 0.05$) for the three investigated periods. The Fe concentration in plants from T2 and T8 decreased by 75 % after three months growing in shale and then increased 4.6 times after five months of waste water application (1.1 times if

Table **3.1**: The effects of presence of *Phragmites* and different inlet concentrations on $H_2PO_4^-$, NH_4^+ - N, NO_3^- - N, pH, E_h and temperature; (n = 2).

Parameter	Summer		Autumn		Winter		Spring	
	High/low	Planted /unplanted	High/low	Planted /unplanted	High/low	Planted /unplanted	High/low	Planted /unplanted
$H_2PO_4^-$	ns	$p < 0.01$	ns	$p < 0.01$	ns	$p < 0.01$	$p < 0.05$	$p < 0.01$
NH_4 - N	ns	$p < 0.01$	ns	$p < 0.01$	ns	$p < 0.01$	$p < 0.05$	$p < 0.01$
NO_3 - N	$p < 0.05$	$p < 0.05$	ns	$p < 0.05$	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$
pH	$p < 0.05$	ns	ns	ns	ns	ns	ns	ns
Eh	$p < 0.05$	ns	ns	ns	ns	ns	$p < 0.01$	$p < 0.01$
t	ns	$p < 0.01$	ns	ns	ns	ns	ns	$p < 0.05$

Table **3.2**: Elemental analysis of plant material harvested prior to planting, after 3 months growing in shale, and after 5 months of waste water application

Element/DM (concentration)	Prior to planting (March 1995)	After 3 months growing in shale		After 5 months of receiving waste water application	
		T2&T8	T4&T6	T2&T8	T4&T6
DM* %	60.3	29.2 (± 0.14)	36.5 (± 5.10)	32.4 (± 3.07)	31.9 (± 4.56)
N %	1.8	1.9 (± 0.14)	1.5 (± 0.71)	1.5 (± 0.14)	1.6 (± 0.32)
P %	0.2	0.1 (± 0.02)	0.1 (± 0.05)	0.1 (± 0.06)	0.1 (± 0.01)
Fe ppm	262.0	65.5 (± 6.15)	69.7 (± 10.87)	300.8 (± 24.80)	345.6 (± 24.00)
Mn ppm	43.8	221.3(± 14.60)	294.5 (± 47.53)	280.1 (± 23.80)	313.1 (± 39.90)
Cu ppm	5.7	13.3 (± 2.00)	10.4 (± 3.39)	4.3 (± 0.03)	6.1 (± 1.70)
Zn ppm	119.0	35.3 (± 0.57)	32.7 (± 4.92)	23.2 (± 5.23)	32.6 (± 3.22)

DM* = dry matter; the plants were in a very poor state (very dry and apparently close to wilting) when obtained for the experiments and this is presumed to be the reason why dry matter content was so high prior to planting.

compared with the value prior to planting); in T4 and T6 it followed a similar pattern. The Mn concentration in T2 and T8 increased 5 fold after growing in shale for three months, and then by a further 30 % after 5 months of waste water application; in T4 and T6 it increased slightly more. The Zn concentration decreased by over 70 % and then declined still further after a further 5 months. The Cu values doubled, then decreased to about the starting concentration but the result was not statistically significant. In addition, an orange, oxidised iron colour was observed on the root surfaces. These results indicate the possibilities of *Phragmites australis* for the removal of Fe and Mn from waste water (Drizo *et al*, 1997). Plants showed extremely good growth and root development in the shale substrate (Appendix 2), achieving a high total surface area for Fe, Mn and P uptake and deposition.

After the plants were harvested in January 1996, total P and N uptake by above - ground biomass was found to be 2.25 g m^{-2} and 26.2 g m^{-2}, respectively (55 kg P ha^{-1} y^{-1} and 640 kg N ha^{-1} y^{-1}). These values were in accordance with the values of 50 to 150 kg P ha^{-1} $year^{-1}$ and 200 to 2500 kg N ha^{-1} y^{-1} suggested by Brix (1994b). However, it should be taken into account that much of the nutrients accumulate in the roots and rhizomes (Hiley, 1995) and therefore it is likely that the actual plant uptake was much higher (Section 3.4).

The contribution of plants to P and N removal was also assessed through the estimate of both P and N input-output CWS's balances, for the period July 1995 - January 1996 (from the start of the experimental period until the plants were harvested) and these values are presented in Tables 3.3 and 3.4. However, it should be noted P and N input-output balances might have been affected by the very unusual N/P ratio of the synthetic sewage (Section 3.2.1). Had the inlet NH_4^+-N input concentration been higher, it is expected that more N would have been assimilated in CWS, via plant and

microbial uptake. On the other hand, these are temporary storage mechanisms, and nitrogen can be released from the system following plant senescence unless removed by harvesting (Section 1.7.5.5).

Table **3.3**: Phosphorus mass balance for the period of 23rd July 1995-7th January 1996 † based on measurements from the greenhouse tanks fed by high concentrations. Quantities in final column ('*unaccounted for*') are presumed to be attached to the substrate. Errors cited represent standard deviation (SD).

	P input kg ha^{-1} ($H_2PO_4^-$-P)	P output kg ha^{-1} ($H_2PO_4^-$-P)	Aboveground plant biomass* kg P ha^{-1}	*Unaccounted for* kg P ha^{-1}
Planted tanks	986.8 ± 9.6	18.9 ± 2.1	22.5 ± 1.6	945.4 ± 5.9
Unplanted tanks	986.8 ± 9.6	39.4 ± 4.2	0	947.4 ± 5.4

* measured as total P % in the plant tissue; † from the start of experiment to plant harvest.

Table **3.4** - Nitrogen mass balance for the period of 23rd July 1995-7th January 1996 based on measurements from the greenhouse tanks fed by high concentrations. Quantities in final column ('*unaccounted for*') may have been taken up by the substrate or volatilised. Errors cited represent standard deviation (SD).

	N input kg ha^{-1} (NH_4^+-N+NO_3^--N)	N output kg ha^{-1} (NH_4^+-N+NO_3^--N)	Aboveground plant biomass* kg N ha^{-1}	*Unaccounted for* kg N ha^{-1}
Planted tanks	503.0 ± 8.4	5.6 ± 1.6	262.5 ± 1.2	234.9 ± 4.7
Unplanted tanks	503.0 ± 8.4	173.5 ± 4.5	0	329.5 ± 3.9

* measured as total N % in the plant tissue.

3.3.2.2. Oxygen release from *Phragmites australis*

After 25 days there was no significant difference in the growth achieved (average height between 0.70 and 0.80 m, maximum 0.95 m) among non-sealed and sealed pots. However, in the non-sealed pots there was an obvious development of new young culms (average height 0.21 m) and approximately 10 new shoots per pot, whereas there was no development of new shoots or young culms in the sealed pots. In addition, an obvious yellowing of existing plants was observed in all sealed pots, which might have been caused by the use of paraffin as a seal. Dissolved oxygen concentrations for all 4 treatments (pots planted with *Phragmites*, the control, pots planted with *Phragmites* and sealed with paraffin and the control sealed with paraffin) are presented in Figure 3.8, below:

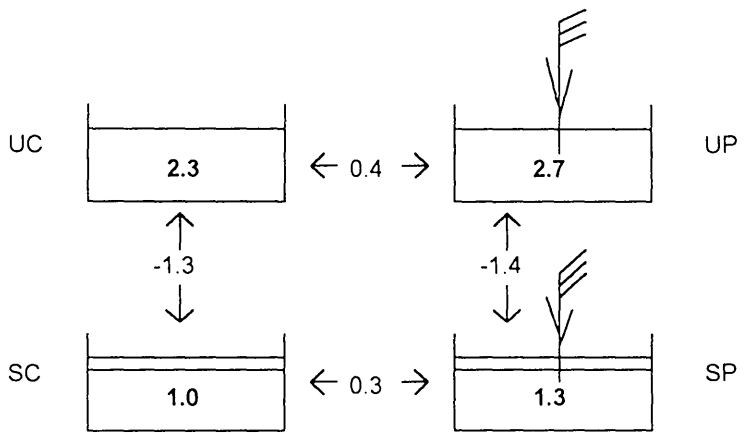


Figure 3.8: The average concentration of oxygen present in four different treatments. UC = unsealed control; SC = sealed control; UP = unsealed planted; SP = sealed planted (units are g O_2 m^{-3}). Oxygen electrode used for measurements was calibrated in a zero oxygen solution.

The paraffin seal reduced the average O_2 concentration by 1.3 - 1.4 g m^{-3}, while the presence of the plants enhanced it by 0.3 - 0.4 g m^{-3} presumably by diffusion through the aerenchyma. The amount of oxygen transferred from the atmosphere to the rhizomes was only 0.002 g m^{-2} day^{-1} , which was much smaller than values reported

in the literature (Section 1.7.5.5). However, it should be noted that this was just a preliminary investigation and that the presence of the paraffin seal might have affected the results.

3.4 Discussion

The experimental set-up was devised to investigate the efficiency of the pilot-scale CWS based on shale with both planted and unplanted tanks and at two different input nutrient concentrations. Although a deterioration of CWS performance with increase in the inlet loading rates has been documented (Section 1.7.4.6. and 1.7.5.6) no such behaviour was observed in this experiment. The systems performed just as well at high concentration as at low concentration both in the case of phosphate and of ammonium.

The unplanted constructed wetlands (which all used horizontal subsurface flow) showed a very high removal of P of 97% throughout the whole period of investigation, 11 months, with the addition of plants contributing an improvement of just 2% to 99%. The fact that the substrate remained equally effective after 11 months of monitoring, even though the inlet loading rates on the four tanks (T3, T5, T4 and T6) receiving the double inlet load had been increased 3 - fold (from 40 to 120 g m^{-3}, i.e. 0.8 - 2.4 g P m^{-2} day^{-1}) for the final month, emphasises the potential of shale to adsorb phosphate. Moreover, although in the vertical column experiment (Chapter 2, Section 2.3) shale showed a P adsorption capacity of 0.65 - 0.73 g P kg^{-1}, the P adsorption in the pilot-scale systems reached 0.85 g P kg^{-1} (unplanted) and 0.87 g P kg^{-1} (planted) and the tanks were still not saturated, which further suggests that this material may be very suitable as a substrate for constructed wetlands. The discrepancy between P adsorption capacity in the vertical columns experiment and pilot-scale

CWS could be attributed to the differences in the experimental set-up (Section 2.2.2.3 and 3.2.1). In particular, while shale packed in the vertical columns was fed with the synthetic sewage only, the pilot-scale CWS were initially fed with real sewage in order to develop a microbial population to resemble a full-scale system, which might have allowed a larger microbial uptake in the latter systems.

The P mass balance, based on the total input and output P loading rates for the period July 1995 - January 1996 (Table 3.3) showed that the difference in P output between planted and unplanted tanks (19.6 kg ha^{-1}) was very similar to the P uptake by the aboveground plant biomass (22.5 kg ha^{-1}), which represented only 2% of the total inlet loading. This is in accordance with the results reported by Brix (1994b; 1997) who stated that the amounts of nutrients that can be removed by harvesting is generally insignificant compared to the loadings in the waste water entering the CWS. Even taking into account that the production of the underground root and rhizome tissue may exceed that of the aboveground standing crop and that more than 50 % of the nutrients is stored in this portion of the plants (Debusk and Ryther 1987; Reddy and Debusk 1987) their overall contribution to P removal would increase by only 2 - 3 % of the total entering the system. Therefore the results suggest that plants account only for a small portion of the removed P and that majority of the P removal was due to incorporation into biological films (microbial uptake) and/or physico-chemical reactions with the substrate. However, P uptake by microbes represents only a short-term removal mechanism and once the steady state is reached, desorption back to the water column takes place, releasing back 35 - 75 % of the adsorbed P (Richardson and Craft, 1993; Kadlec and Knight, 1995). This implies that most of the P which has been removed from the system over the period of 5.5 months has participated in some physico-chemical reaction with the substrate.

In the determination of the P and N balances it should be taken into account that evapotranspiration rates were not measured, and therefore the estimation of the quantities leaving the system, based only on concentration measurements, would have been too low.

The nitrogen mass balance, based on the total input and output N loading rates for the period July 1995 - January 1996 (Table 3.4) showed that the output of mineral N (NH_4^+ - N + NO_3^- - N) from the unplanted tanks (173.5 kg ha^{-1}) represented only 34.5% of the total inlet loading. The remaining 65.5% (329.5 kg N ha^{-1}) could have been retained in the unplanted tanks through several possible mechanisms. For example, it could have been adsorbed by the substrate through cation exchange (Platzer and Netter, 1994; Wittgren and Maehlum, 1997). Zhu and Sikora (1995) estimated that 61% of NH_4^+ - N that had been removed from the unplanted gravel-based CWS was due to adsorption on the substrate. In addition, mineral N could have also been immobilised in the microbial cells, but similarly to the P uptake by these organisms, most of the N taken up by this process can be released again to the water column (Kadlec and Knight, 1995). Another possibility for N removal in the unplanted tanks may have been nitrification at the air-water interface where O_2 could have been supplied to nitrifiers via diffusion in a 1-2 cm layer with production of NO_3^- (Mitsch and Gosselink, 1993; Hammer and Knight, 1994; Sikora *et al*, 1995). However, as the observed concentrations of NO_3^- - N (Figure 3.5) were always extremely low, the results suggest that either nitrification rates were extremely low or denitrification occurred at a rapid rate once NH_4^+ - N was nitrified. Indeed, the oxygen release experiment (Section 3.3.2.2) showed that the oxygen supplied through the plant roots might have been insufficient to support nitrification. Since approximately 4.6 g O_2 is needed to oxidise 1 g of NH_4^+ - N (Hiley, 1995; Sikora *et al*, 1995) oxygen deficiency is frequently mentioned as a reason for the poor N removal performance of the CWS

employing subsurface flow (Hammer and Knight, 1994; Platzer and Netter, 1994; Green *et al*, 1997).

In contrast to P, mineral N (NH_4^+ - N + NO_3^- - N) removal via aboveground plant biomass accounted for just over 50% of the total N input loading rates (Table 3.4) 262.5 kg ha^{-1} being removed in this way over the whole period of investigation. Similar results were observed in the study of a gravel based subsurface CWS conducted by Sikora *et al* (1995). The differentiation between plant uptake and other mechanisms of NH_4^+ - N removal is difficult because the rates of these processes and the below ground biomass uptake were not evaluated. However, if it is hypothesised that at least an amount of N, equal to the above ground biomass N, was immobilised in the rhizosphere, all of the uncounted N removal might be attributed to plants. Platzer and Netter (1994) pointed out that, due to the large number of factors that affect N removal via CWS, it is difficult to quantify the influence of each factor separately.

Despite the fact that plants are believed to have an influence on substrate temperature by acting as an insulation layer and by providing additional surface area for the development of microbial activity (Wood, 1990), their effect on effluent temperature was apparent only on two occasions in this study (Table 3.1). Moreover, variations in pH, Eh and temperature values at the outlets did not account for the variations in either P or N removal (Section 3.3.1, Fig. 3.6 and 3.7) either in planted or unplanted tanks. These results indicate that the processes which were removing phosphate or ammonium were not negatively or positively affected by the changes in the measured parameters for the range of values measured in the tanks.

3.5. Conclusions

The results in this chapter develop the investigations of the previous chapter in two directions. First, the experimental scale is increased to a pilot scale CWS, to investigate the potential of shale for nutrient removal from waste water in a more realistic setting. Second, the effectiveness of shale is analysed, not only with respect to P removal, but also with respect to the removal of ammonium and nitrate.

The experiments again confirmed the effectiveness of shale. It was almost fully effective in removing P (with or without plants) and, in combination with *Phragmites*, it was also effective in removing N. Moreover, the saturation levels predicted in Chapter 2 were exceeded, indicating that the potential performance of shale might be even better than previously thought.

Results from the pilot-scale CWS performance predict that a full scale shale based CWS could have a very good performance for both P and N removal. The results of the performance of the greenhouse tanks suggest that if BOD and SS are removed at the primary stage of wastewater treatment, the high efficiency in nutrient removal is achievable. This finding is in comformity with the studies carried out by Hiley and Warell in 1998 (P. Hiley, pers. comm.).

Chapter 4: Phosphate and ammonium distribution in constructed wetlands with horizontal subsurface flow, using shale as a substrate[3]

4.1. Introduction

As outlined in Section 1.7.3, wetland performance data are often generated from the actual measurements of what was coming into and out of the constructed systems. Theoretical removal models based on such data have been developed principally for biological oxygen demand (BOD) and suspended solids (SS) removal, with the suggestion that the same kinetics can be applied for reduction of ammonium (Kadlec *et al*, 1993; Hammer and Knight, 1994; Kadlec, 1995; Reed *et al*, 1995; Bavor *et al*, 1995). The form of the model used by all these workers involves an exponential decrease in pollutant concentrations to a background value approaching zero along the transect from wetland inlet to wetland outlet. The model can be expressed as follows (Section 1.7.3):

$$q \frac{dC}{dx} = -k (C-C^*) \qquad (1)$$

where

q = hydraulic loading rate defined as the ratio of the inflow (Q, $m^3\ d^{-1}$) and the surface area (A, m^2); x = fraction of distance from inlet to outlet; C = pollutant concentration of the system ($g\ m^{-3}$); C^* = background pollutant concentration ($g\ m^{-3}$); k = first order area-based reduction rate constant ($m\ d^{-1}$).

---

[3] This chapter is based on a paper entitled 'Phosphate and ammonium distribution in constructed wetlands with horizontal subsurface flow, using shale as a substrate' , to be submitted to *Water Research*.

An alternative approach, based on the concept of water retention time has been formulated by Kadlec and Knight (1996):

$$\frac{Cx - C^*}{Ci - C^*} = e^{-k_v T x} \qquad (2)$$

where k_v = first order volumetric reduction rate constant (d^{-1}); x = fractional distance through the wetland; T = retention time (days).

Theoretical wetland models tend to be system - specific, because of the lack of data and understanding of the key mechanisms involved in the removal processes (Bavor, *et al.*, 1995). The engineering design of CWS is often based on predictable or assumed sets of conditions rather than on real data. For example, very few studies take into account the influence of geometric configuration or depth of water or media on the systems' performance efficiency (Reed, 1991). Cooper and Green (1995) emphasised the need for collecting data in order to obtain more information on pollutant distribution within the CWS, especially during cold and potentially freezing weather.

In the present study, an attempt has been made to collect a data set on spatial distribution of nutrients within the liquid phase in the CWS. It is believed that this kind of information on influent distribution and physical configuration of the systems will lead to improved design of systems in the future (Tchobanoglous, 1987). Concentrations of phosphate ($H_2PO_4^-$), ammonium (NH_4^+) and nitrate (NO_3^-), were measured in water samples taken at various depths (0.1m, 0.2 m and 0.35 m) and lengths (0.2, 0.4, 0.6 and 0.8 m) from the inlets towards the outlets, in a greenhouse CWS over a period of 11 months. These data were used to test the theoretical model of removal (see equation 1). Although their influence on nutrient removal was not observed in the long-term CWS performance (Chapter 3), redox potential (E_h), pH

and temperature were also measured. In addition, the contribution of *Phragmites australis* to these processes was assessed.

4.2. Methods

Vertical sampling points (plastic tubes, diameter = 0.008 m) were placed at 0.2, 0.4, 0.6 and 0.8 m from the inlet along the length of each tank (described in the previous chapter, Section 3.2) and at three different depths: 0.35 m (bottom of the tanks), 0.2 m and 0.1 m below the substrate surface (Figure 3.1). In addition, a fibre glass rod was placed in each tube in order to prevent it from filling with water between sampling, which might cause mixing of water from the different layers during sampling. Once a month, waste water samples were taken from each of the observation points, using 50 ml syringes.

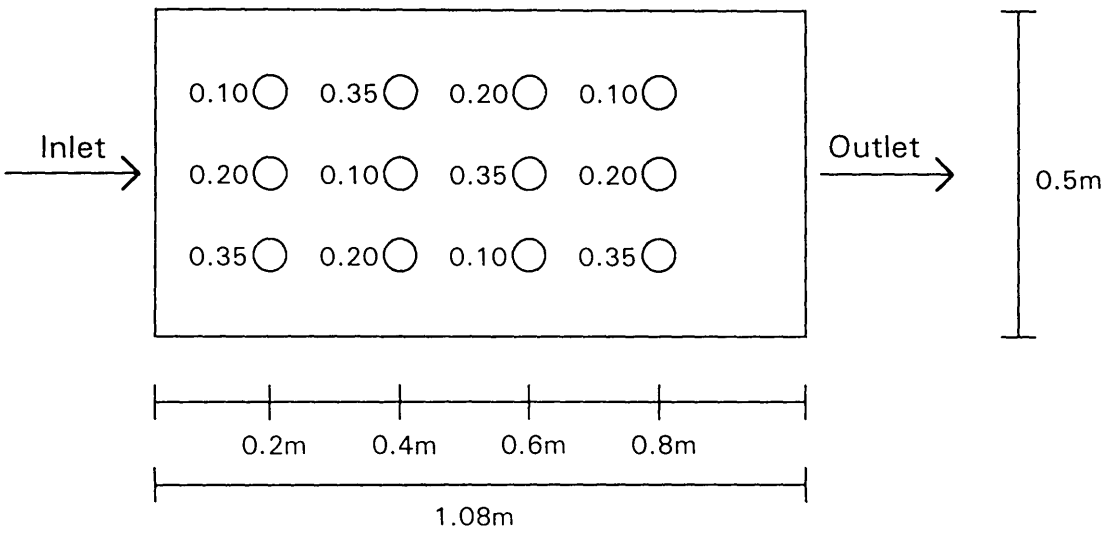


Figure 4.1: Locations of the sampling points in a greenhouse tanks, plan view.

After 10 months, the inlet concentration of phosphate was increased three-fold (120 g m^{-3}), and that of ammonium two-fold (40 g m^{-3}), with the aim of reaching saturation of the substrate. However, even at such a high inlet concentration, shale had such a

high capacity for phosphate removal that saturation of the substrate was not reached (See Chapter 3, p 70).

$H_2PO_4^-$ was determined using a spectrophotometer (model SP6 - 500 UV, Pye Unicam, Cambridge, England; limits of detection at 0.2 g m^{-3}) according to the standard ammonium molybdate method (DoE, 1980). NH_4^+ was measured using the method devised by Crooke and Simpson (1971) and NO_3^- by the method described by Best (1976) using a Chemlab Instruments Ltd continuous flow analyser with limits of detection between 0.1 - 0.2 g m^{-3}. pH and E_h values were measured by standard techniques (Rowell, 1994), using a conventional glass electrode, a reference calomel electrode and a platinum electrode. Temperature was measured using a combined oxygen electrode and temperature recorder.

4.3. Results

4.3.1. Phosphate distribution

Data from planted and unplanted tanks are presented on separate figures for clarity (Figures 4.2. and 4.3 respectively). $H_2PO_4^-$ concentrations showed a very rapid decrease from inlet to outlet in the planted tanks. Values were extremely low (between 0.5 - 1 g m^{-3}) at all depths and all lengths during the first 8 months of investigation, rising to 3 g m^{-3} in May 1996 (Figure 4.2.). In the unplanted control systems, higher values of P were observed, especially at 0.2 m and 0.4 m lengths (1.5 times planted values), the highest tending to be at the bottom of the tanks (0.35 m) (Figure 4.3). However, despite being fed with extremely high P input concentrations of 20 - 40 g m^{-3}, both planted and unplanted systems achieved removal of 90 - 98 %,

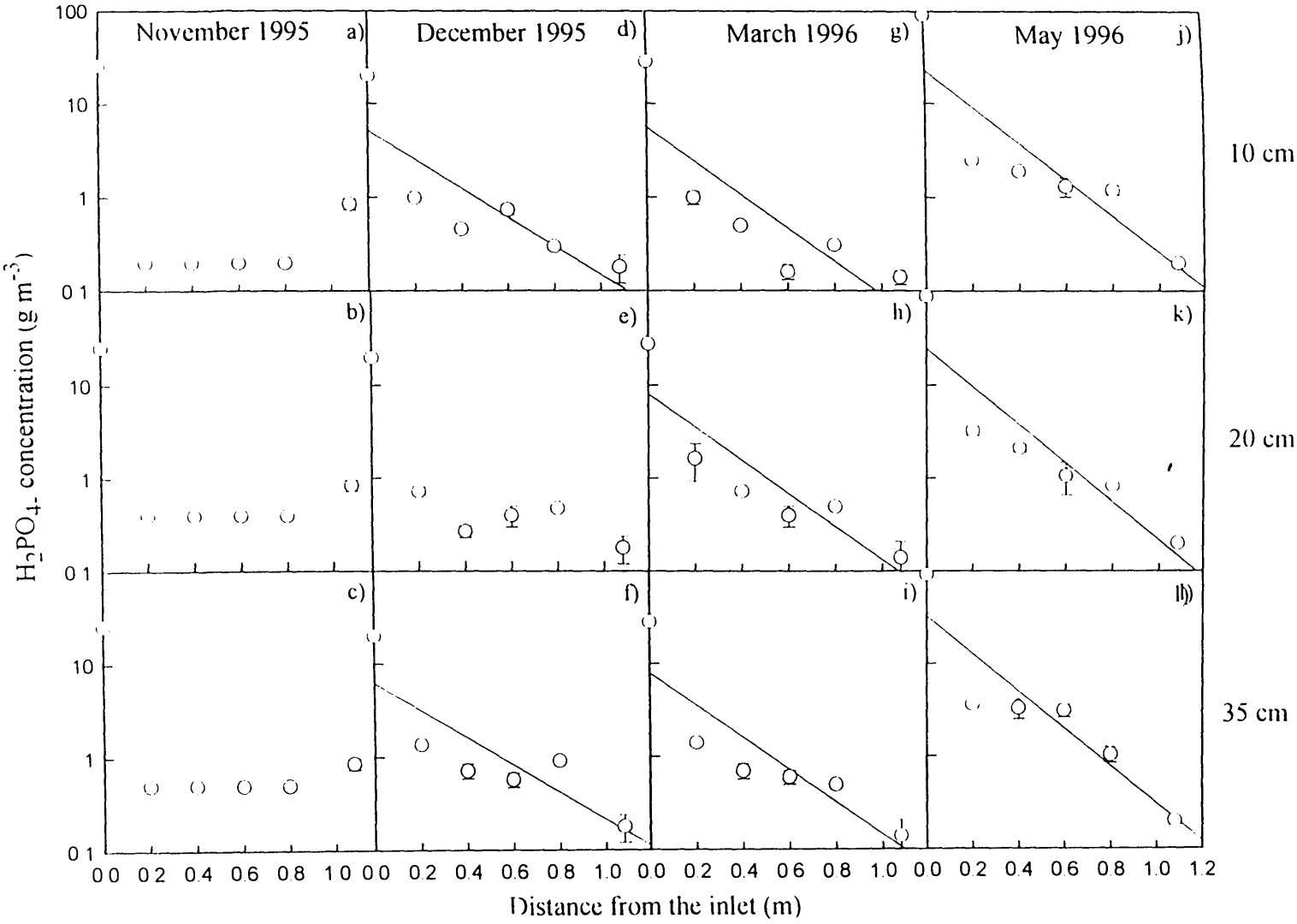


Figure 4.2: Spatial distribution of $H_2PO_4^-$ - P within a liquid phase in the planted tank (o) for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD). Fitted line represents the relationship between $H_2PO_4^-$ - P concentration and distance from the inlet.

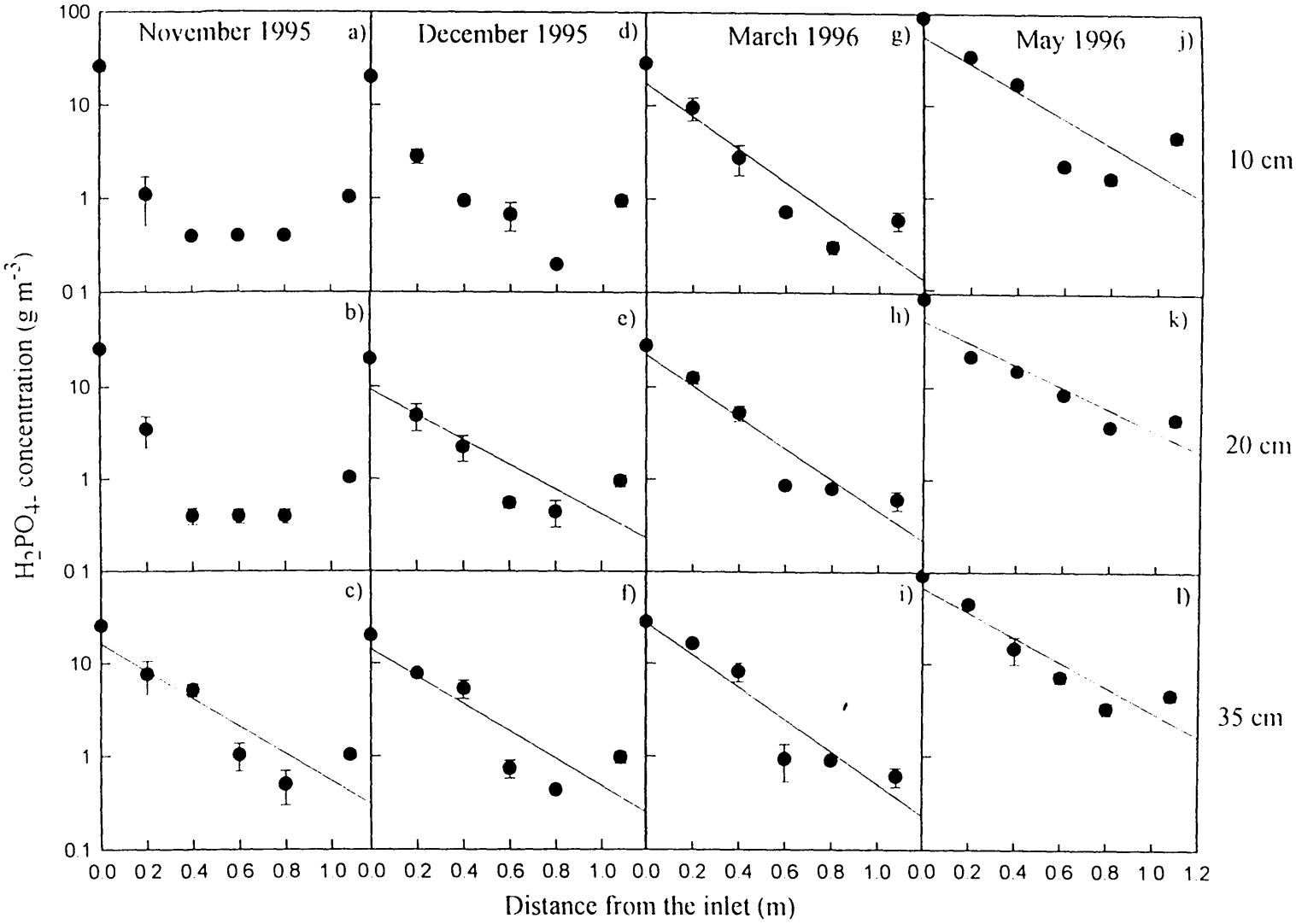


Figure 4.3: Spatial distribution of $H_2PO_4^-$ - P within a liquid phase in the unplanted tank (●) for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

and this was true even when the input concentration was increased to values as high as 120 g m^{-3} towards the end of investigation in May 1996.

In order to test the effects of depth, distance from the inlet and presence of plants on P distribution, split plot analyses of variance with tanks treated as main plots were performed (Sokal and Rohlf, 1981), using SAS Stat statistical software (SAS Institute, 1985). The effect of depth on P concentration was significant ($p < 0.01$) in both planted and unplanted tanks throughout the period of investigation, with concentrations being higher at the bottom of the tanks (Table 4.1, Figures 4.2 and 4.3). The effect of distance from the inlet was also significant on all sampling occasions, in both planted and unplanted tanks, with concentrations decreasing as distance increased ($p < 0.01$, Table 4.1). The presence of plants had a significant effect at all depths and distances throughout the experiment.

P concentrations were plotted on a logarithmic scale to test whether the decrease with distance from the inlet was exponential. In planted tanks this was true in eight out of twelve cases, while in unplanted in nine out of twelve. Regression lines are presented on Figures 4.2 and 4.3, while the associated correlation coefficients, regression equations and rate constants k (see equation 1) are displayed in Tables 4.2a and 4.3 b. The rate constants k for unplanted and planted tanks were compared for each sampling occasion, using a t - test. A significant difference ($p < 0.02$) occurred only on the last sampling occasion, in May, with rate constants being higher in the planted tanks.

Table 4.1: Results of Split Plot Analysis of Variance on the effects of depth, distance from the inlet (length), and presence of *Phragmites australis* on $H_2PO_4^-$, NH_4^+ - N, NO_3^- - N, Eh, pH and temperature; (n = 48).

Parameter	November (4 months)			December (5 months)			March (8 months)			May (10 months)		
	D	L	P/u	D	L	P/u	D	L	P/u	D	L	P/u
$H_2PO_4^-$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$	$p < 0.01$
NH_4^+ - N	$p < 0.05$	$p < 0.01$	$p < 0.01$	ns	$p < 0.01$	$p < 0.01$	ns	$p < 0.01$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$
NO_3^- - N	ns	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.01$	$p < 0.01$	ns	$p < 0.01$	$p < 0.05$	ns	$p < 0.05$	$p < 0.01$
pH	$p < 0.01$	$p < 0.01$	ns	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.05$	ns	ns	ns	$p < 0.02$	$p < 0.01$
Eh	ns	$p < 0.05$	$p < 0.01$	$p < 0.05$	$p < 0.01$	$p < 0.05$	nc	$p < 0.01$	$p < 0.01$	ns	$p < 0.01$	$p < 0.01$
t	ns	$p < 0.01$	$p < 0.01$	ns	ns	$p < 0.01$	$p < 0.01$	$p < 0.01$	ns	ns	ns	$p < 0.01$

D = depth; L = length; P/u = planted/unplanted;

Table 4.2 a: Regression lines, correlation coefficients and rate constants k (m d^{-1}) for $H_2PO_4^-$ - P in unplanted tanks.

Depth	November	December	March	May
10			log (P) = - 1.76 x + 1.24 r = 0.915 p < 0.02 k = 0.081	log (P) = - 1.47x + 1.75 r = 0.841 p < 0.05 k = 0.062
20		log (P) = - 1.34 x + 0.98 r = 0.845 p < 0.05 k = 0.062	log (P) = - 1.69 x + 1.35 r = 0.948 p < 0.01 k = 0.078	log (P) = - 1.19 x + 1.72 r = 0.930 p < 0.01 k = 0.055
35	log (P) = - 1.47 x + 1.21 r = 0.897 p < 0.02 k = 0.068	log (P) = - 1.47 x + 1.16 r = 0.878 p < 0.02 k = 0.068	log (P) = - 1.74 x + 1.44 r = 0.945 p < 0.01 k = 0.080	log (P) = - 1.35 x + 1.85 r = 0.935 p < 0.01 k = 0.068

Table 1a: Regression lines, correlation coefficients and rate constants k (m d^{-1}) for $H_2PO_4^-$ - P in planted tanks.

Depth	November	December	March	May
10		log (P) = - 1.54 x + 0.72 r = 0.844 p < 0.05 k = 0.071	log (P)= - 1.79 x + 0.75 r = 0.832 p < 0.05 k = 0.082	log (P) = - 1.94 x + 1.35 r = 0.880 p < 0.05 k = 0.089
20			log (P)= - 1.78 x + 0.91 r = 0.891 p < 0.02 k = 0.082	log (P)= - 2.06 x + 1.40 r = 0.912 p < 0.02 k = 0.095
35		log (P) = - 1.46 x + 0.79 r = 0.847 p < 0.05 k = 0.067	log (P) = - 1.73 x + 0.90 r = 0.885 p < 0.02 k = 0.080	log (P)= - 2.02 x + 1.51 r = 0.918 p < 0.01 k = 0.093

4.3.2. Ammonium distribution

NH_4^+ - N concentrations followed a similar trend of rapid decrease from inlet to outlet in planted tanks (Figure 4.4). Values were very low (below 2.5 g m^{-3}) during the first eight months of wastewater application at all lengths and depths, but then gradually increased to almost 5.0 g m^{-3} between months 8 and 10 (which still presented 87.5 % reduction when compared with the input load rates). The levels of NH_4^+ - N in unplanted systems were relatively high at 0.2 m, 0.4 m and 0.6 m lengths throughout the experiment, and rose from 10 - 15 g m^{-3} in November to 20 - 30 g m^{-3} in May 1996, the latter representing only a 25 % reduction.

In order to test the effects of depth, distance from the inlet and presence of plants on NH_4^+ - N distribution, split plot analyses of variance with tanks treated as main plots were performed (Sokal and Rohlf, 1981), using SAS Stat statistical software (SAS Institute, 1985). The effect of depth was significant on two sampling occasions, in November 1995 and May 1996 (Table 4.1). The effect of distance on NH_4^+ - N distribution was significant throughout the experiment, with lower concentrations at greater distance ($p < 0.01$, Table 4.1). In addition, the presence of plants had a significant effect ($p < 0.01$) at all depths and distances, planted tanks having the lower concentrations throughout the period of investigation (Table 4.1).

Similarly to P, NH_4^+ - N concentrations were plotted against distance from inlet on a logarithmic scale and these data for both unplanted and planted tanks are presented on Figure 4.4. Regression lines show that N concentration in unplanted tanks decreased exponentially with respect to distance throughout the experiment, while in planted tanks this was the case in nine out of twelve occasions. Tables 4.3 a and 4.3 b show the associated correlation coefficients, regression equations and rate constants k.

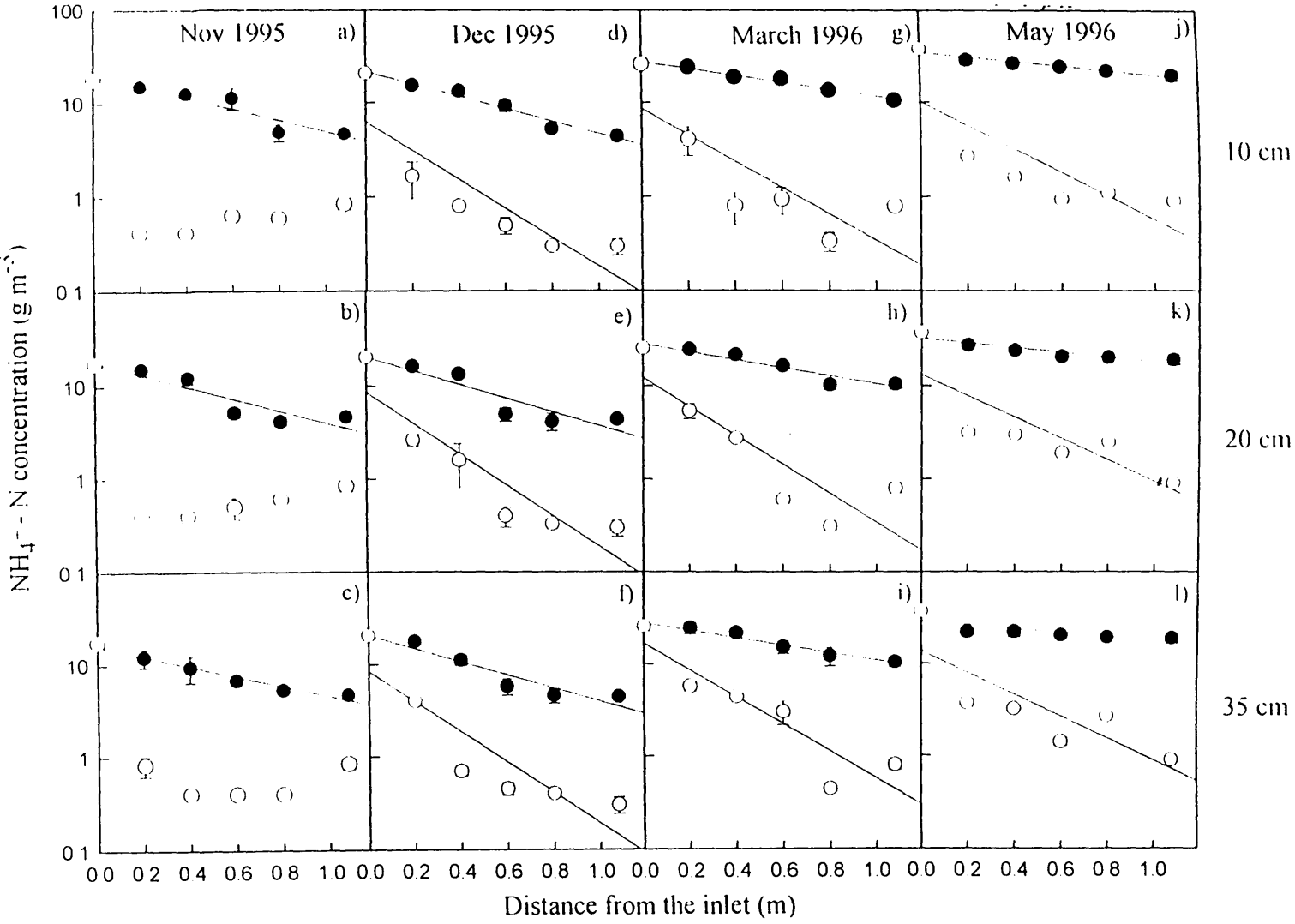


Figure 4.4: Spatial distribution of NH_4^+ - N within a liquid phase in the unplanted (●) and planted (o) tank for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

Table 4.3 a: Regression lines, correlation coefficients and rate constants k (m d^{-1}) for NH_{4+} - N in unplanted tanks

Depth	November	December	March	May
10	log (N) = - 0.59 x + 1.29 r = 0.943 p < 0.01 k = 0.027	log (N) = - 0.65 x + 1.33 r = 0.983 p < 0.01 k = 0.030	log (N) = - 0.37 x + 1.43 r = 0.986 p < 0.01 k = 0.017	log (N) = - 0.25 x + 1.53 r = 0.967 p < 0.01 k = 0.010
20	log (N) = - 0.65 x + 1.26 r = 0.920 p < 0.01 k = 0.030	log (N) = - 0.73 x + 1.31 r = 0.925 p < 0.01 k = 0.034	log (N) = - 0.43 x + 1.45 r = 0.948 p < 0.01 k = 0.020	log (N) = - 0.26 x + 1.51 r = 0.918 p < 0.01 k = 0.012
35	log (N) = - 0.55 x + 1.20 r = 0.981 p < 0.01 k = 0.025	log (N) = - 0.72 x + 1.32 r = 0.954 p < 0.01 k = 0.033	log (N) = - 0.40 x + 1.44 r = 0.976 p < 0.01 k = 0.018	log (N) = - 0.22 x + 1.47 r = 0.860 p < 0.05 k = 0.012

Table 4.3 b: Regression lines, correlation coefficients and rate constants k (m d^{-1}) for NH_{4+} - N in planted tanks.

Depth	November	December	March	May
10		log (N) = -1.53 x + 0.80 r = 0.873 p < 0.05 k = 0.075	log (N) = - 1.39 x + 0.94 r = 0.815 p < 0.05 k = 0.064	log (N) = - 1.25 x + 1.0 r = 0.822 p < 0.05 k = 0.058
20		log (N) = - 1.65 x + 0.94 r = 0.916 p < 0.02 k = 0.076	log (N) = - 1.56 x + 1.10 r = 0.868 p < 0.05 k = 0.072	log (N) = - 1.15 x + 1.12 r = 0.833 p < 0.05 k = 0.053
35		log (N) = - 1.64 x + 0.92 r = 0.896 p < 0.02 k = 0.070	log (N) = - 1.46 x + 1.22 r = 0.917 p < 0.02 k = 0.080	log (N) = - 1.19 x + 1.14 r = 0.839 p < 0.05 k = 0.055

In order to test whether there was a significant difference in rate constants between planted and unplanted tanks, t-test was performed for each sampling occasion, using Sigmastat statistical software (Kuo *et al.*, 1992). It showed that there was a significant difference ($p < 0.01$) throughout, with constants being higher in the planted tanks.

4.3.3. Nitrate distribution

The input load of NO_3^- - N was extremely low (0.5 - 1.0 g m^{-3}) and consequently, the concentrations remained low at all lengths and depths of the system throughout the experiment, often falling to 0.1 g m^{-3}, which was at the limits of detection of the instrument (Figure 4.5). Decrease in concentrations from the inlet towards the outlet was 15 % and 30 % in unplanted and planted tanks respectively, but this was not statistically significant.

Similarly to $H_2PO_4^-$ - P and NH_4^+ - N, split plot analysis of variance with tanks treated as main plots were performed (Sokal and Rohlf, 1981). It showed that the effect of depth had a significant influence on nitrate distribution only on one sampling occasion, in December 1995 (Table 4.1). A tendency for concentrations to be 30 % higher in planted than in unplanted tanks at 0.2 m and 0.35 m depth (the depths where the roots and rhizomes are largely found) and first 0.5 m length from the inlet was observed. The effect of distance and the presence of plants were apparent throughput the period of investigation (Table 4.1).

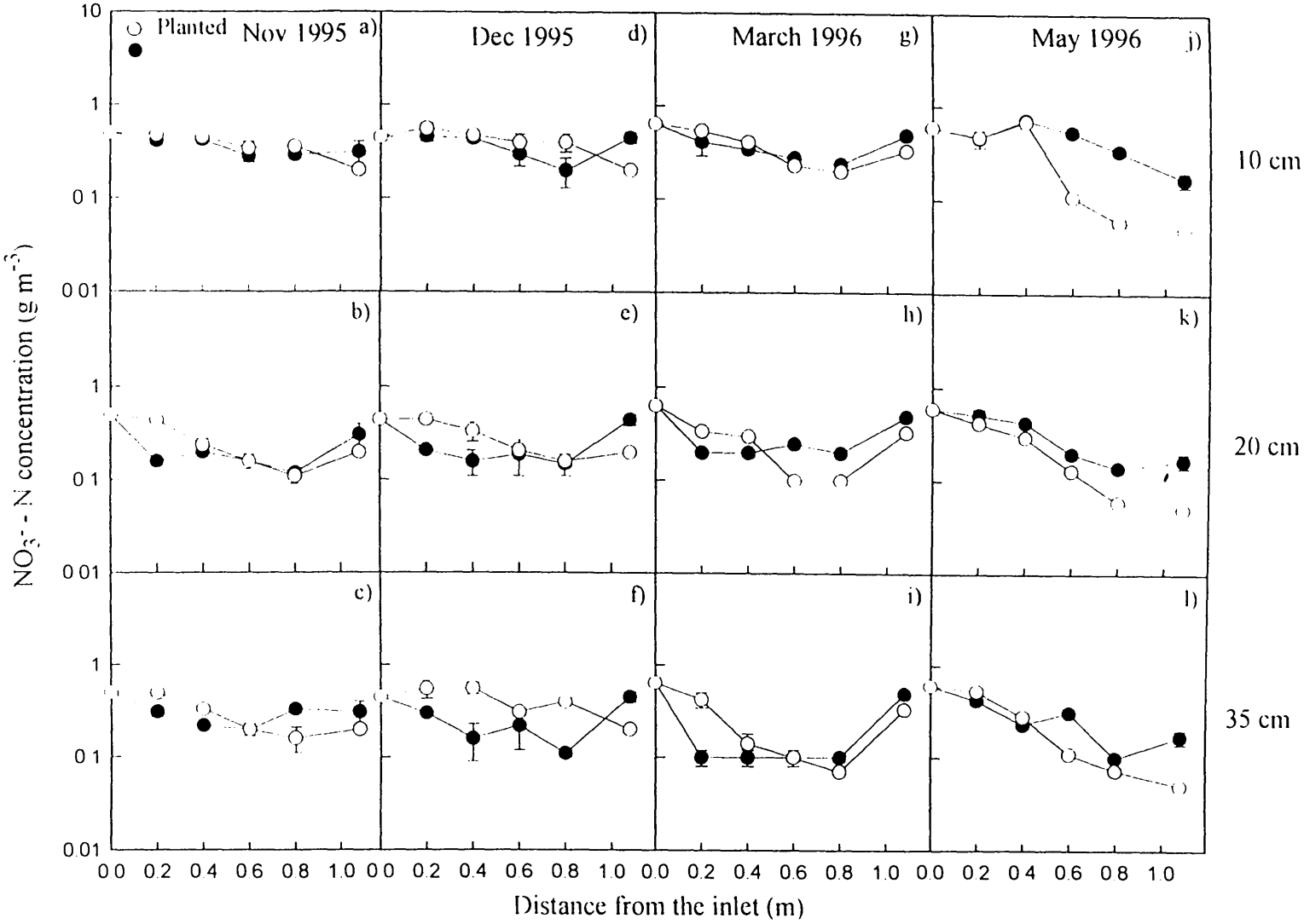


Figure 4.5: Spatial distribution of NO_3^- - N within a liquid phase in the unplanted (●) and planted (o) tank for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

4.3.4. Eh, pH and temperature distribution

Redox potentials (E_h) were fairly stable ranging from 60 to 120 mV, except in December 1995, when values fell to 20 - 50 mV (Figure 4.6) The Split plot analysis of variance showed that different depths did not have a significant influence on potential values, except on one sampling occasion, in December 1995. On the other hand, the effect of length was clear ($0.01 < p < 0.05$) with an increase in values along the transect from the inlets towards the outlets. Planted tanks showed significantly higher redox potential throughout the period of investigation ($0.01 < p < 0.05$; Table 4.1).

pH values ranged from 5.5 to 6.5 being fairly stable at all depths and along all lengths of the tanks (Figure 4.8). There was a significant effect of depth, except on one sampling occasion in May 1996. The effect of distance was also apparent throughout, except on one sampling occasion in March 1996. In addition, the effect of plants was apparent on two sampling occasions, in December 1995 and in May 1996 (Table 4.1).

Temperature values ranged between 6.6 and 14.9 ^{o}C with values remaining above 5 ^{o}C even in December, when outside temperature values decreased to below 0^{o}C (Figure 4.9). The effect of depth was significant only on one, while the effect of length was significant at two sampling occasions (November 1995 and March 1996). The effect of plants was apparent at all depths and along all lengths of the systems, except on one sampling occasion, in March 1996 (Table 4.1).

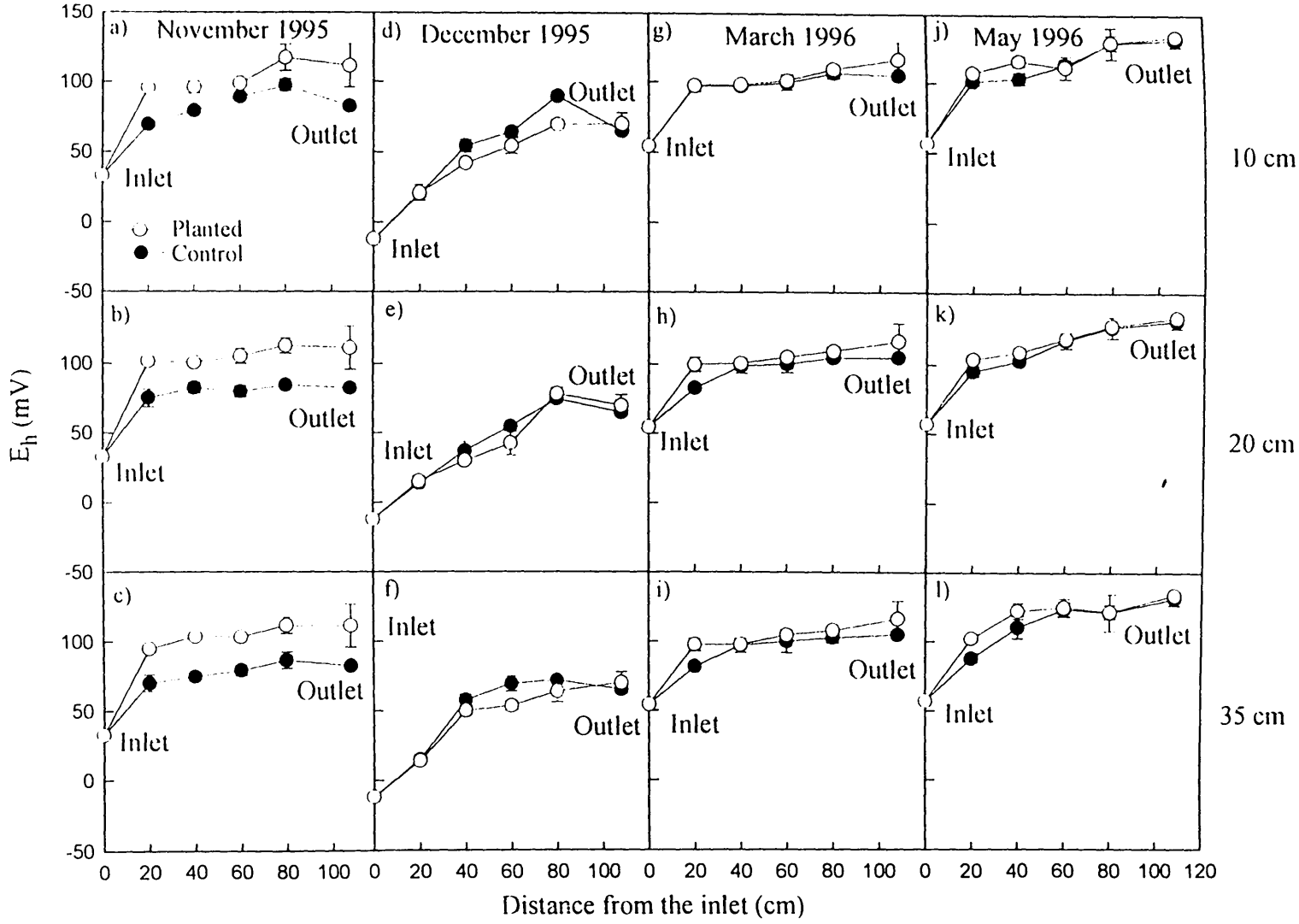


Figure 4.6: Spatial distribution of E_h within a liquid phase in the unplanted (●) and planted (o) tank for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

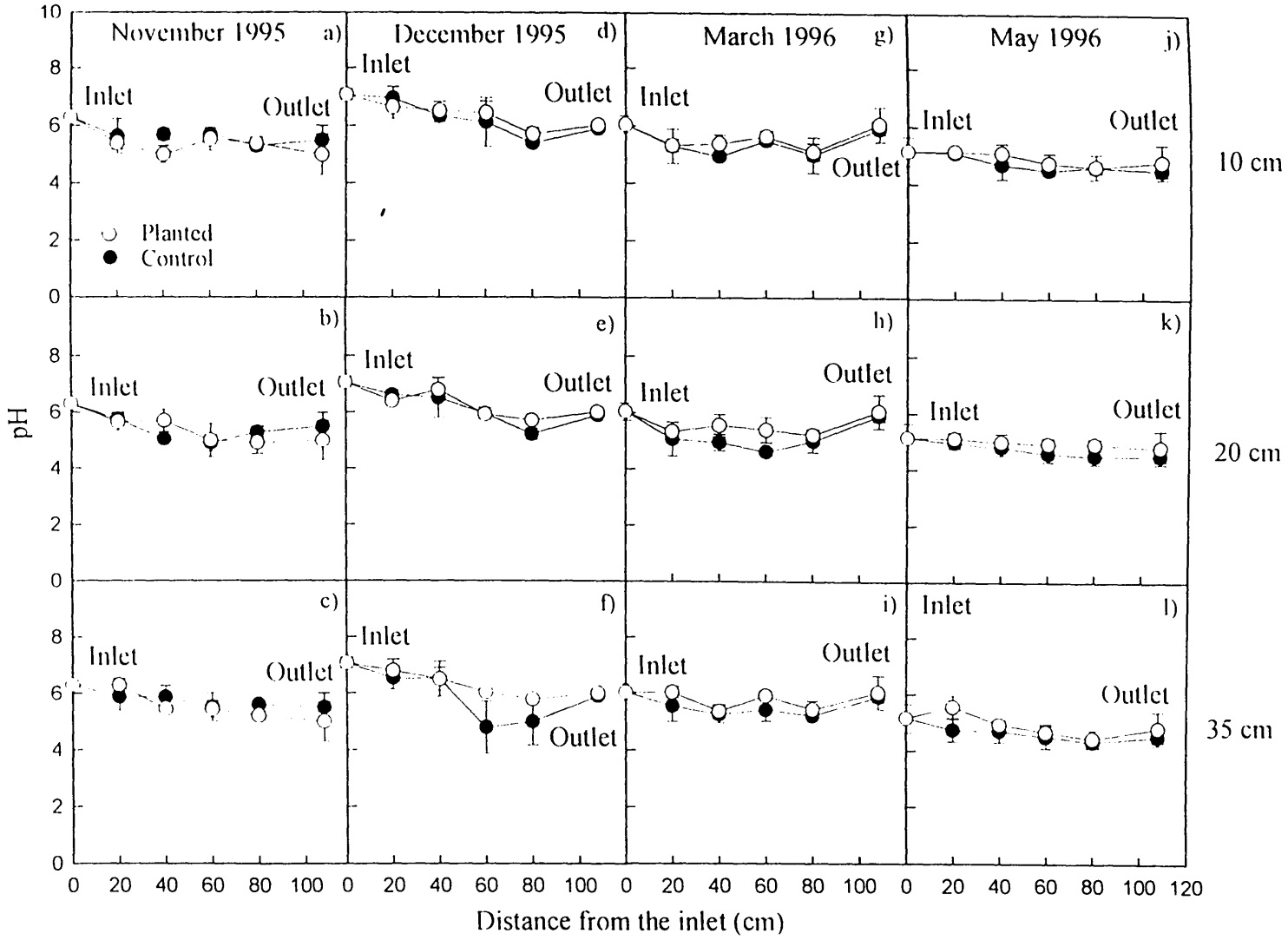


Figure 4.7: Spatial distribution of pH within a liquid phase in the unplanted (●) and planted (o) tank for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

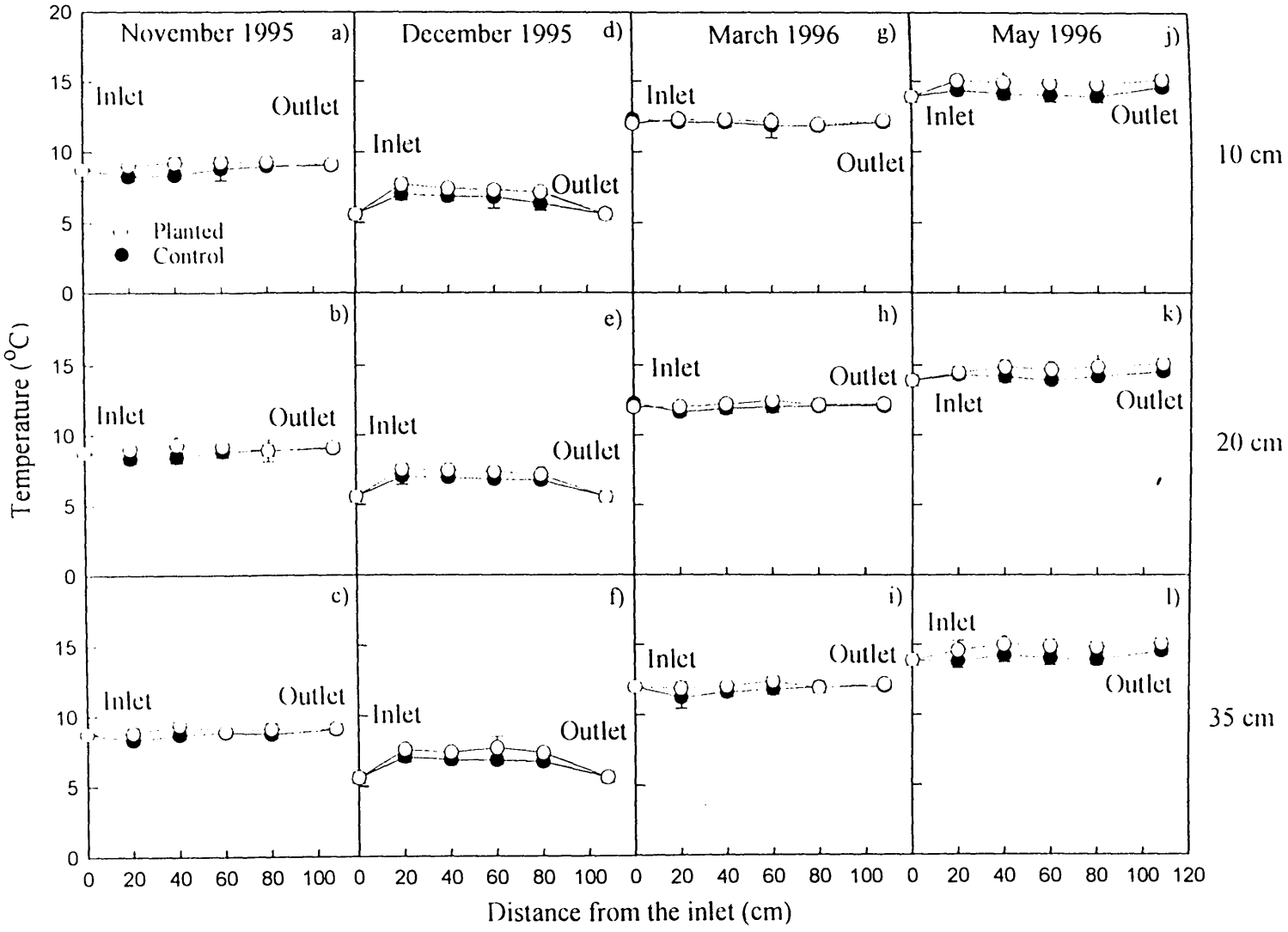


Figure 4.8: Spatial distribution of temperature within a liquid phase in the unplanted (●) and planted (o) tank for the period Nov 1995 - May 1996. Vertical bars denote standard deviation (SD).

4.4. Discussion

The exponential decrease in P concentrations from the inlet towards the outlet conforms well with the equation (1). The pattern was similar in both unplanted and planted tanks, the latter showing a more rapid reduction, in particular in the 0.2 m distance from the inlet. In both, the decrease could be a time effect: wastewater near the inlet has been in the system for less time than wastewater near the outlet, so has had less interaction with substrate and plant roots.

That there was no significant effect of depth is in agreement with equation (1) which assumes that flow at depth h and rate Q move through the constructed wetland under steady uniform conditions (Reed *et al.* 1988; Bavor *et al*, 1989; Reed *et al.* 1995). However, it could also be attributed to the fact that the systems were relatively shallow (0.35 m as opposed to the usual 0.6 m recommended by the European Guidelines (EC/EWPCA, 1990)) as it is well emphasised that equation (1) implies simpler conditions than actually occur in practice (Kadlec, 1993; Bavor *et al*, 1995; Buchberger and Shaw, 1995).

The tendency for rate constants to be higher in planted tanks (Table 4.2a and b) in March and May 1996 could be attributed to the enhanced plant uptake of P at the beginning of the growing season. The rate constants were statistically different (Section 4.3.1) only in May 1996, probably due to a three-fold increase in input loading rates. Overall, rate constants were slightly higher than typical values of $k = 12$ m y^{-1} ($k = 0.033$ m d^{-1}) reported by Kadlec and Knight (1996). However, it should be taken into account that values given by Kadlec and Knight (1996) were calculated for full scale systems and different hydraulic loading rates.

The fact that the treatment efficiency remained extremely high throughout (95 - 98%), with virtually complete removal of P by the time the wastewater reached the outlet can be explained by a very high P adsorptive capacity of shale (0.65 - 0.7 g P kg^{-1}) obtained in laboratory investigations (Chapter 2). In addition, the current study indicates that the P adsorptive capacity of shale is even higher than previously thought, reaching 0.84 g P kg^{-1} and 0.87 g P kg^{-1} in the unplanted and planted tanks respectively. This increase could be attributed to the precipitation reactions on the shale surfaces resulting from the E_h and pH interactions.

Redox potential (E_h) influences P transformations within CWS through Fe reduction. Values of E_h below 130 mV cause the reduction of Fe^{3+} to Fe^{2+}, and the release of associated P could be expected (Gambrell *et al*, 1991). That the release has not been observed could be explained by the transformation of crystalline Fe and Al minerals to the amorphous form, the latter having a higher P sorption capacity which may precipitate as insoluble Fe - or Al - phosphates resulting in an overall increase in shale CWS P removal capacity (Section 1.7.4.1).

An exponential decrease in NH_4^+ - N concentrations along the transect from the inlet to the outlet was in accordance with the theoretical models developed by Hammer and Knight, (1994), Bavor *et al*, (1995) and Reeds *et al.* (1995), and, as with P removal, contact time may play a major role in their distribution within CWS. The rate constants in planted tanks were on average 3 times higher than those of unplanted (Table 4.3a and b) due to a more rapid reduction of ammonium in the planted tanks. Under reduced conditions, NH_4^+ - N is stable and may be adsorbed by the substrate or used by plants and micro-organisms (Sikora *et al*, 1995). The results from this study show that overall ammonium reduction in unplanted tanks represented only 25 - 45 %. The efficiency was probably limited by relatively slow rates of nitrification.

The removal of N in wetland systems is largely dependent on input loading rates resulting in up to 70% removal efficiency at rates of between 20 - 30 g N m^{-2} y^{-1} but decreasing in efficiency at higher loading rates (Faulkner and Richardson, 1989). The fact that virtually all N was removed in planted tanks, even when loading rates were doubled towards the end of the experiment, is encouraging.

As planted tanks showed more rapid reduction in nutrient concentrations, with the rate constants being significantly higher in particular in the case of N ($p < 0.01$), the theoretical removal model (1) could be refined to:

$$C_{out}/C_{in} = \exp [- (k_p + k_s)T] \qquad (2)$$

where:

k_p would represent the rate constant of the plants, and k_s the rate constant of the substrate.

In the case of unplanted tanks, the equation of both P and N removal is simplified to:

$$C_{out}/C_{in} = \exp (- k_s T) \qquad (3)$$

As the measurements in Figures 4.2, 4.3 and 4.4 are taken with respect to the distance from the inlet, it is necessary to convert between the residence time and the distance. The overall residence time from inlet to the outlet is 5 days, and assuming a steady flow, this gives a mean plug flow velocity of 0.2 m day^{-1} and thus, the equation can be written as:

$$T = l/v = 5l \qquad (4)$$

where *l* presents the distance from the inlet to the point of measurements; v = velocity of the liquid phase in a CWS; Therefore the equation relating nutrient concentrations and distance in unplanted tanks becomes:

$$C_{out}/C_{in} = \exp(-5k_S l) \qquad (5)$$

The experimental data from this study are consistent with the exponential model. It would be interesting to obtain further results confirming the model.

Input loading rates of nitrate were extremely low in this study (0.5 - 1 g m^{-3}) and therefore the results should be treated with caution. Nitrate is unstable in reduced zones and is quickly depleted as a result of assimilative reduction and denitrification (Section 1.7.5.4). These processes support the development of a concentration gradient for the diffusive flow of NO_3- from the surface oxidised layer around the roots to the reduced zones where the denitrification process effectively converts nitrate to molecular dinitrogen (Patrick and Reddy, 1976; Faulkner and Richardson, 1989). The fact that the planted systems showed only a 10 % increase in nitrate concentrations would suggest that the amount of O_2 which can be released from the plant rhizosphere, creating the oxidised zones in an otherwise anaerobic environment, is not sufficient to support the nitrification processes (Brix, 1994; Hiley, 1995).

The low redox potentials (between 20 and 150 mV) reflect the reduced state of the substrate. The rate and magnitude of E_h depends on the amount of organic matter, the nature and content of the electron acceptors, the temperature and the duration of submergence. The increase in E_h values along the transect from length 0.4 m to the outlets is associated with the reductions in H_2PO_4-, NH_4+ - N and NO_3- - N values indicates that between 0.4 and 1 m there was a transition to more oxidising conditions

within the substrate. The higher potentials in planted beds might have been created by an increase in the biomass of roots and rhizomes combined with the radial diffusion of oxygen (Reddy and D'Angelo, 1997).

pH values were fairly constant, ranging between 5.5 and 6.5, which is typical for submerged acidic substrates high in organic matter and reducible iron. pH value affects hydroxide, carbonate, phosphate and silicate equilibria in submerged environments and may have significant implications in wastewater treatment as they regulate the precipitation and dissolution of solids, adsorption and the concentration of Fe^{2+}, Al^{3+} and S^{2-} ions (Ponnamperuma, 1972).

There was no evidence of length or depth differences in temperature in either planted or unplanted tanks. The insulation effect of plants and the high microbial activity could have attributed to explained the higher temperatures (0.5 - 1 ^{o}C) observed in planted tanks (Wood, 1990). The beneficial effect of vegetation in a subsurface CWS's winter performance has been shown in several studies (Maehlum *et al*, 1995; Yin and Shen, 1995).

4.5. Conclusions

Data on geometrical configuration of this kind are valuable in providing guidelines for wetland design. A system with an aspect ratio of 2:1 supported a gradient in pollutants through the longitudinal profile with up to 95 % of the nutrient removal achieved within the first 0.2 m (1/5 of the total length) in planted tanks. It is still difficult to say whether results obtained from this pilot scale study, set up in a greenhouse, are representative of larger scale systems. However, they provide a better

understanding of the nutrient distribution and removal processes that take place within the CWS.

An important observation was made that the wastewater percolated to the full depth in both planted and unplanted systems, providing sufficient contact with the substrate to achieve high P and N removal rates throughout the period of investigation (between 95 - 98% in both planted and unplanted systems and 85 - 90 % in planted systems respectively). This confirmed results from a previous investigation (Chapter 3) that such systems can be used as a highly efficient wastewater treatment option with the potential to treat effluents to the tertiary standards after a single year of operation.

The rate constants for P and N removal processes were slightly higher than those reported by other authors, but this is not surprising, as the latter were calculated for full-scale systems.

Chapter 5: Investigation of hydraulics and flow regime in constructed wetlands with horizontal subsurface flow, using bromide tracer

5.1. Introduction

Hydraulic residence time (T) represents one of the most important parameters in the design of constructed wetlands (Watson and Hobson, 1989; Moshiri, 1993; Cooper, 1996). It is defined as the average time that wastewater remains in the bed travelling from the inlet end to the outlet end (Watson and Hobson, 1989; Sanford *et al.*, 1995).

Typical values of T for subsurface flow systems vary between 2 and 7 days (Knight, 1994; Wood, 1995). In order to simplify calculations, it is oftent assumed that wastewater flows uniformly through all of the pore spaces and that the whole of the bed volume participates in the treatment process (Cooper, 1993; Sanford *et al.*, 1995; Reed and Brown, 1995). However, several researchers have found that constructed wetlands do not exhibit ideal uniform flow behaviour and have reported the occurrence of preferential flows and short-circuiting (Bowmer, 1987; Schierup *et al.*, 1990; Kadlec, 1993; Netter, 1994; Buchberger and Shaw, 1995). Kadlec *et al.* (1993) and Kadlec (1994) stated that the flows are typically in the transition region between laminar and turbulent and that contact times between the wastewater and the substrate often differ from the theoretical retention time calculated from the wetland empty volume and the volumetric flow rate.

One major problem frequently reported when evaluating the performance of constructed wetlands is the clogging of the substrate (especially if the substrate is soil or sand), resulting in overland flow and bypassing of the treatment zone within the matrix and rhizosphere of the plants (Brix, 1987; Schierup *et al.* 1990; Conley *et al.*

1991). The characteristics of the substratum material have a substantial effect on the hydraulics of the wetland system. The material provides the physical support matrix to promote plant growth and root development, while at the same time presenting a porous medium through which the wastewater flows and is subjected to the activity of microorganisms (Fisher, 1990; Hammer, 1992). If short cuts and dead zones occur within the substratum in a wetland system, the effective reaction volume and thus the purification efficiency is reduced (Netter, 1994).

Shale was found to be a very efficient substrate for phosphate P removal from wastewater, achieving 98 - 100 % removal of P in both planted and unplanted tanks at the loading rate of 0.02 m d^{-1}. Ammonium N removal in unplanted tanks was between 40 and 75 %, but it was still completely removed in planted tanks (Chapter 3). However, because of its plate-like structure which breaks easily into very thin laminae, there is a possibility that shale may clog up with time. Therefore, a tracer experiment was performed, in which measurements were taken at several locations (distances) and depths within each tank to check whether uniform flow was achieved or whether clogging of the substrate had occurred. In addition, the actual hydraulic residence time of the wetland was measured.

5.2. Methods

Determination of the flow characteristics was carried out using the twelve vertical sampling probes placed in each tank for the purpose of previous experiment (Figure 4.1, Chapter 4).

Different tracers and fluorescent dyes (lithium, bromide, uranin, eosin) have been employed in studying the hydraulic properties of constructed wetlands (Bowmer, 1987; Schierup *et al*, 1989; Kadlec, 1994; King *et al*, 1997). Bromide (Br^-) was

chosen for this experiment because it represents a chemically very stable tracer material of low sorptive properties (Flury and Papritz, 1993). In addition, it showed the highest recovery among the range of tracers used in hydraulic investigations of planted soil filters (Netter, 1994). A solution containing 20 g l^{-1} of Br^- (as KBr) was prepared and 2.5 l were added to each tank, during one working cycle (50 minutes) of the peristaltic pumps. This was carried out in April 1996, 9 months after establishment of the constructed wetlands. The first set of samples was collected from each of the observation points (plus the outlet) one hour after the tracer pulse application, using 50 ml syringes. Samples were then taken once per day for 6 days. Bromide concentrations were determined using an ion-selective electrode (Adriano and Doner, 1982) (see Appendix 3). Flow was maintained at a constant rate, and mean residence time was obtained from plots of tracer concentration versus time at the sampling points.

Netter and Bischofsherger (1990) pointed out that the easiest way to interpret the movement of a tracer through a CWS is by determination of the change in tracer concentration with time, but that this method should only be used if the flow is constant (e.g. if the runoff varies, it should be taken into account as well). A typical concentration versus time curve for a tracer experiment is shown in Figure 5.1:

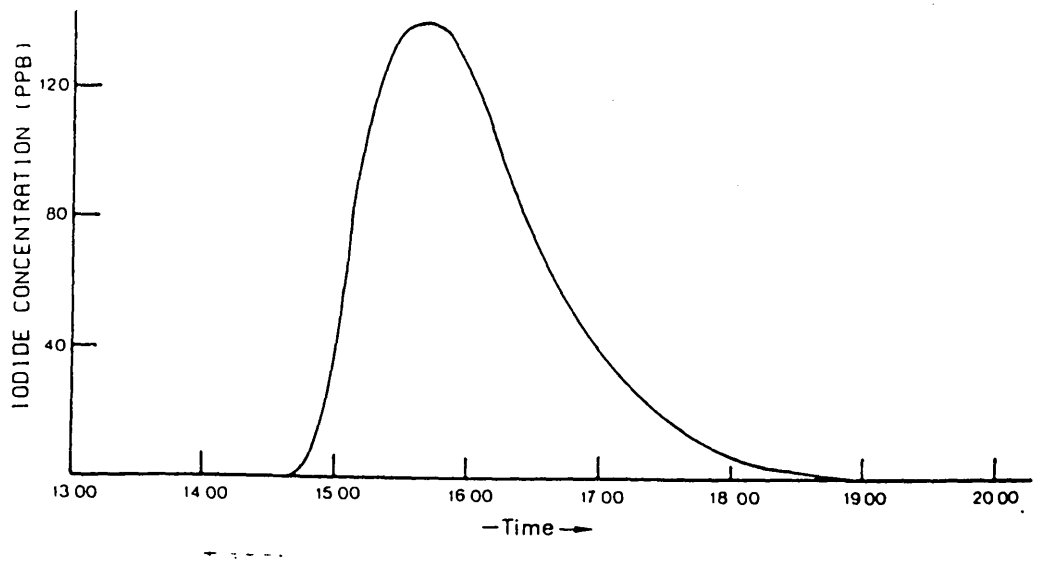


Figure 5.1: Iodide tracer experiment on the Bedford Ouse (Whitehead *et al*, 1986).

5.3. Results

The results of tracer tests revealed that the majority of the wastewater travelled through the bottom of the tanks (Figures 5.2 and 5.3). In both unplanted and planted tanks, there was almost no flow at 10 cm depth below the surface, which was expected, given that the inlet pipe was at the depth of 20 cm (Chapter 3). The observed mean hydraulic residence time at the outlets and at all depths, was approximately 6 days, which was slightly higher than the theoretical residence time (5 days). Although the whole of the pore volume was available for wastewater to pass through, there was a preferential flow through the basal parts in both the unplanted and planted tanks.

In addition, the Br^- peak concentrations fell between 0.8 and 1.0 m, even though at 0.2 m to 0.8 m they were nearly the same in both the unplanted and planted tanks. The overall recovery of bromide tracer was good, representing 88 % in planted and

84 % in unplanted tanks respectively, of which the greatest proportion (66.5 and 65 %) was in the bottom layer. The occurrence of surface flow was not observed.

In order to test the effects of depth and the presence of plants on flow characteristics, two-way ANOVA analyses were performed, using SigmaStat statistical software (Kuo *et al.*, 1992). Each of the treatments had two replicates and tests were performed on absolute values. The results of the analyses showed that there were major hydraulic differences ($0.02 < p < 0.05$) between the bottom of the tanks (35 cm) and the two upper zones (20 and 10 cm) in both unplanted and planted tanks. Although the tracer breakthrough curves follow a similar pattern (Figures 5.2 and 5.3), the difference in Br^- concentrations in planted and unplanted tanks was significant ($p < 0.02$). This implies the presence of different flow characteristics in the unplanted and planted tanks.

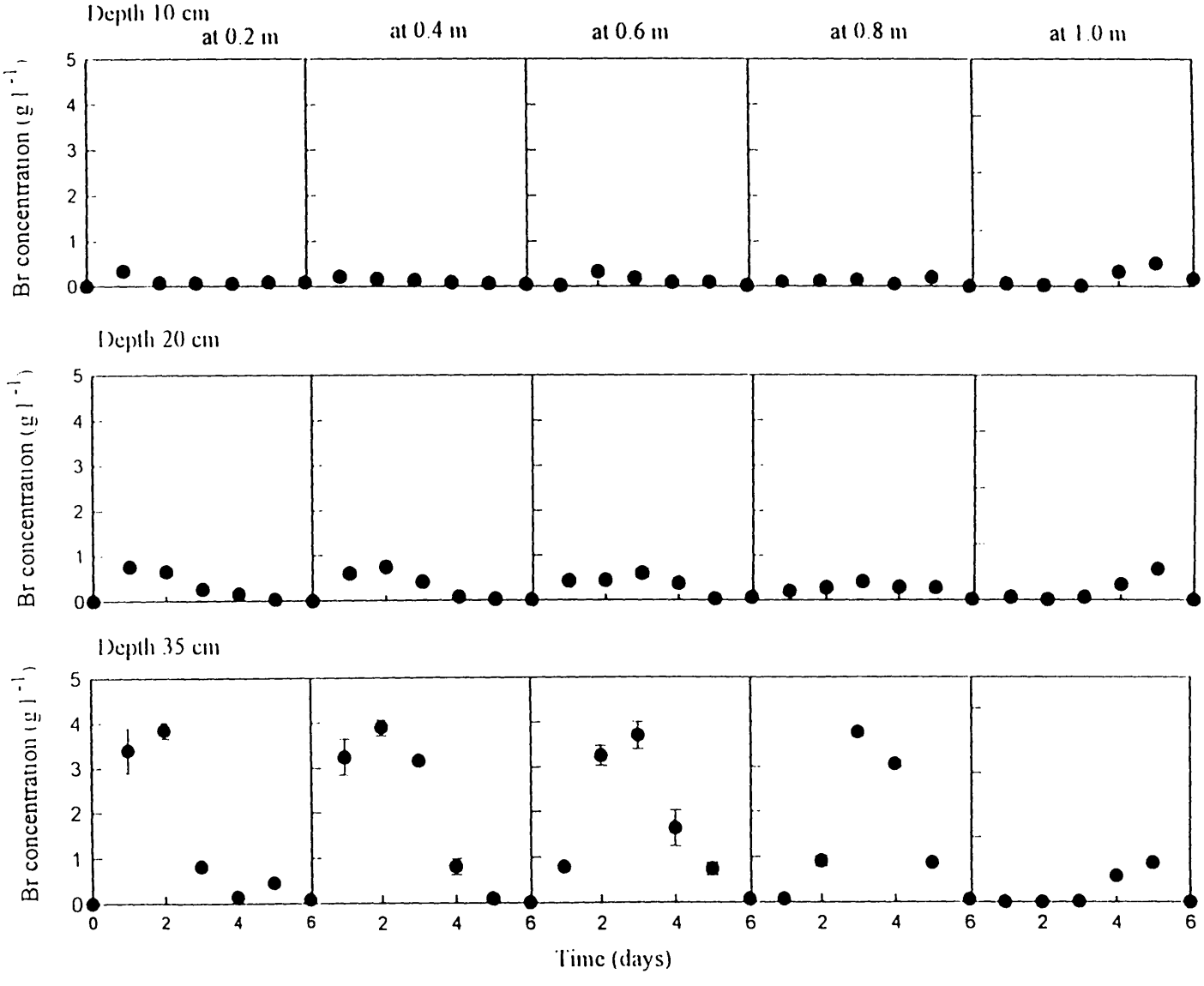


Figure 5.2: Tracer concentration versus time in the unplanted tank (●) for the period 29/03 - 04/04 1996. Vertical bars denote standard deviation (SD)

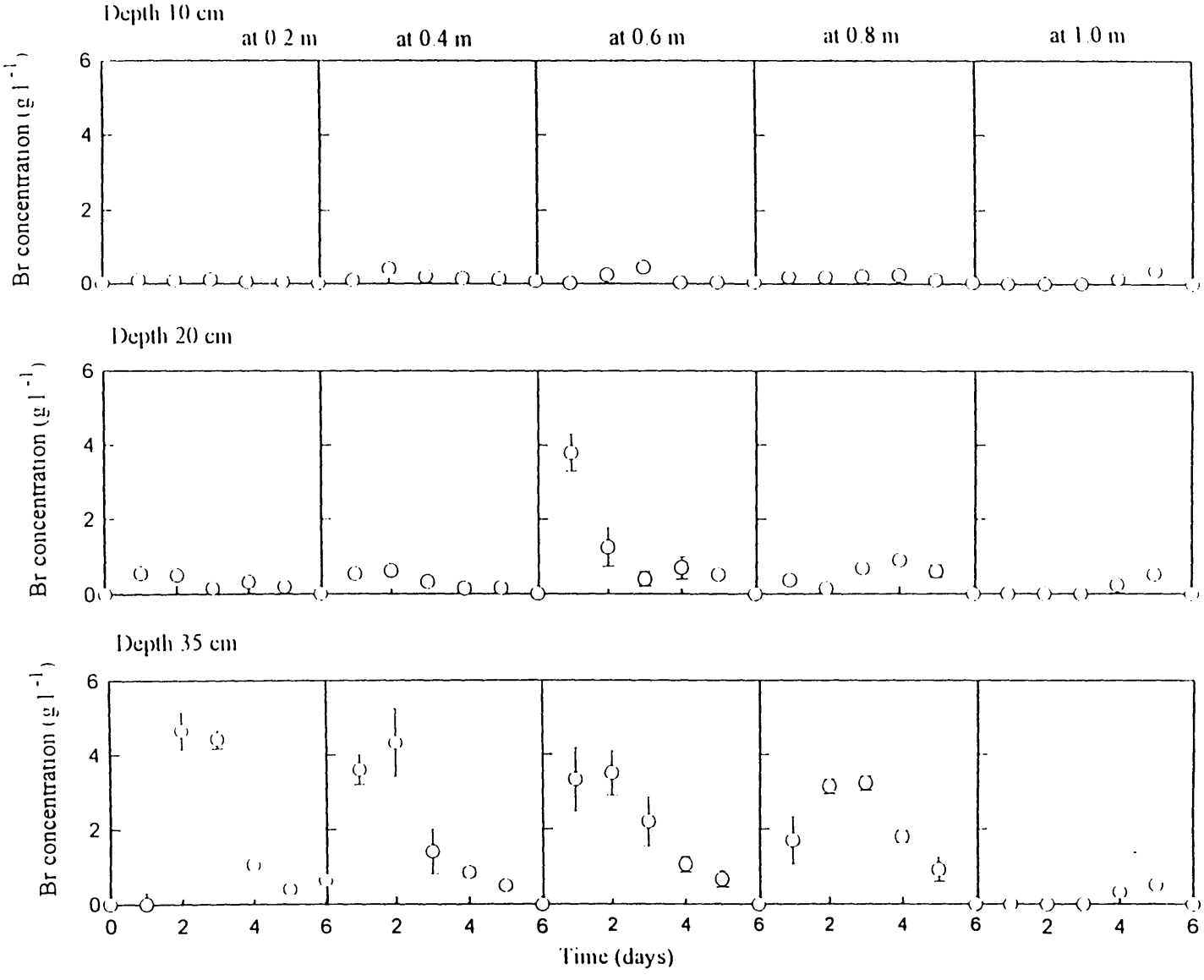


Figure 5.3: Tracer concentration versus time in the planted tank (o) for the period 29/03 - 04/04 1996. Vertical bars denote standard deviation (SD)

5.4. Discussion

The fact that the major portion (65 %) of tracer travelled through the bottom layer in both planted and unplanted tanks suggests the occurence of a preferential flow in this part of the wetland. This could have a two-fold explanation: firstly, the inlet pipe was set at a depth of 20 cm, contributing to the flow attenuation in the upper layer. Secondly, a difference in the density and the way that shale particles were packed inside the tanks at the time of setting up the greenhouse systems could have favoured channelling and the occurrence of preferential flows. If there had been a preferential flow, one would have expected only one third of the wetland pore volume to be available for the wastewater flow, resulting in the actual residence time being shorter then the theoretical one. This would also greatly reduce the treatment efficiency of the systems (Sanford *et al.*, 1995). However, the tracer breakthrough curves in both planted and unplanted tanks show that the actual residence time (Figures 5.2. and 5.3) is equal to the theoretical one (6 days). This discrepancy remains unexplained. In addition, there is no obvious explanation for the rapid fall in Br^- peak concentrations between 0.8 and 1.0 m.

The negative effect that plants may have on the hydraulic regime of the wetlands is reported by several authors (Bowmer, 1987; Breen and Chick, 1995; Marsteiner *et al.*, 1996). Bowmer (1987) suggested that plants may influence system performance through channelling flow around the root mass thus causing short-circuiting. Breen and Chick (1995) studied the rootzone dynamics in constructed wetlands and concluded that root biomass developed in the upper zone of the wetland system naturally directs flow to the lower zone, making it the path of least resistance. Marsteiner *et al.* (1996) hypothesised that plant roots may significantly reduce the porosity and therefore overall retention time in subsurface flow wetlands. However, the fact that the major portion of the flow travelled through the basal regions in both

unplanted and planted tanks in this study suggests that development of root biomass may not necessarily be a major cause of the preferential flows in wetland systems. Other factors such as the location of the inlet zone (Watson and Hobson, 1989; Steiner and Freeman, 1989; Cooper, 1993) or difference in chemical gradients along the wetland (Rogers *et al.*, 1990; Breen and Chick, 1995) should also be taken into account as well.

5.5. Conclusions

The tracer breakthrough curves demonstrated that there was a tendency for wastewater to flow through the basal regions, indicating poor mixing between different layers of the wetland system. This study showed that the actual hydraulic retention time was similar to the theoretical one, which rarely happens in practice. This was partly due to the fact that the evapotranspiration which occurred was not compensated for by any water input by precipitation, thus the water balance was different from that of a full-scale outdoor system.

The flow distribution was similar in both planted and unplanted tanks, suggesting that plant root development in the shale substrate did not reduce the reactive volume of the systems and thus did not have any negative effects on their purification efficiency. In addition, no evidence of clogging was observed. This confirmed the good properties of shale as a substrate found in a previous study (Drizo *et al.*, 1997).

Chapter 6: Phosphate and ammonium removal in the field system

6.1. Introduction

The greenhouse system based on shale as a substrate showed promising results for the removal of phosphate (98% - 100 % in both planted and unplanted systems) and ammonium (95 - 98% in planted and 50 - 75% in unplanted), using a synthetic sewage solution (Chapter 3). Therefore, it was decided to test the shale in a full-scale system using real sewage. This was necessary in order to check whether the results from the small CWS, (with aspect ratio 2:1 and relatively low hydraulic loading rate of 0.0625 $m^3\ m^{-2}\ day^{-1}$) were representative of larger systems. It is well known that small-scale systems (0.5 m wide by 1 m long) maintain the desired flow regime more easily, providing better contact between the influent and the substrate and therefore resulting in higher quality effluent (Cooper and Findlater, 1990; Moshiri, 1993). Moreover, it had to be taken into account that greenhouse systems are protected from outside factors such as precipitation, wind and evapotranspiration and therefore may not have the same hydrological characteristics as an outdoor wetland system. As Kadlec (1987) pointed out, coupling research on greenhouse/laboratory systems with open ecosystems should lead to a better understanding of processes that influence and control nutrient cycling within the wetlands.

Apart from allowing the hydrology of the system to be investigated, information on larger, open systems' performance using shale as a substrate was necessary from the practical point of view as it would enable an estimation of the applicability of shale based systems to be made. As pointed out in previous sections (Chapters 3 and 4), a lot of failures of CWS in the past resulted from insufficient laboratory investigations of the materials chosen as substrates in the CWS. Data on $H_2PO_4^-$, NH_4^+, NO_3^-,TP, TN, pH, redox potential (E_h) and temperature (t) from the field site were expected to provide better insight into the performance of a shale-based system.

6.2. Methods

A full scale wetland system, constructed in 1987 by Fife Regional Council and located on the north bank of the river Forth at Valleyfield, Fife, Scotland (Figure 6.1) was available for the trial to test the suitability of shale material. The position of the site was very important as it lies in the vicinity of the Torry Bay, which is designated as a Site of Special Scientific Interest (SSSI).

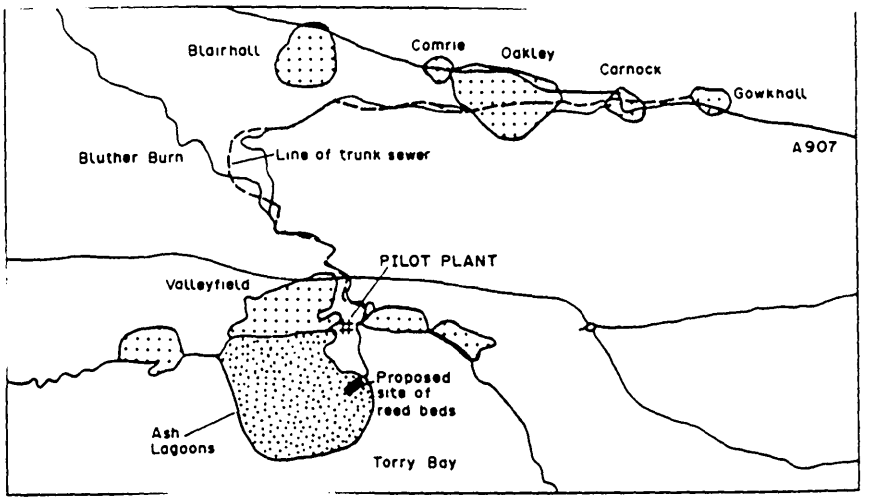


Figure 6.1: Plan of location and sewerage catchment. Source : Wolstenholme and Bayes (1990)

The system was constructed with the aim of removing biological oxygen demand (BOD) and suspended solids (SS). It consisted of four beds (each 10 m long, 4.5 m wide and 0.6 m deep) with a design surface area of approximately 3 m^2 pe^{-1}. The floor of each bed was covered by a plastic liner (Monarflex 500 and 750), necessary to prevent percolation of sewage into the ground water. In addition, gabions (rock-filled wire nets) were placed along the inlet and outlet of each bed to secure an even distribution of the flow through the system (Wolstenholme and Bayes, 1990) (Figure 6.2 shows a simplified plan of the system; Appendix 4 shows a detailed plan). Design criteria were to serve a population equivalent (pe) of 60, with an average flow of crude sewage of 15 m^3 day^{-1}, giving a hydraulic loading rate (flow per unit cross section of the bed) of 0.625 m^3 m^{-2} day^{-1} and nutrient loading rate of 0.083 m^3 m^{-2} day^{-1} (flow per plan area of the bed). This was 10 times and 4 times higher than the

respective rates in the greenhouse systems (Chapter 3, Section 3.2). Flow was provided from a 150 mm diversion pipe from the main sewer which discharged into a combined screen chamber and flow control. The influent fell into a double-acting tipping-trough and discharged into a split chamber to give flow to the four beds.

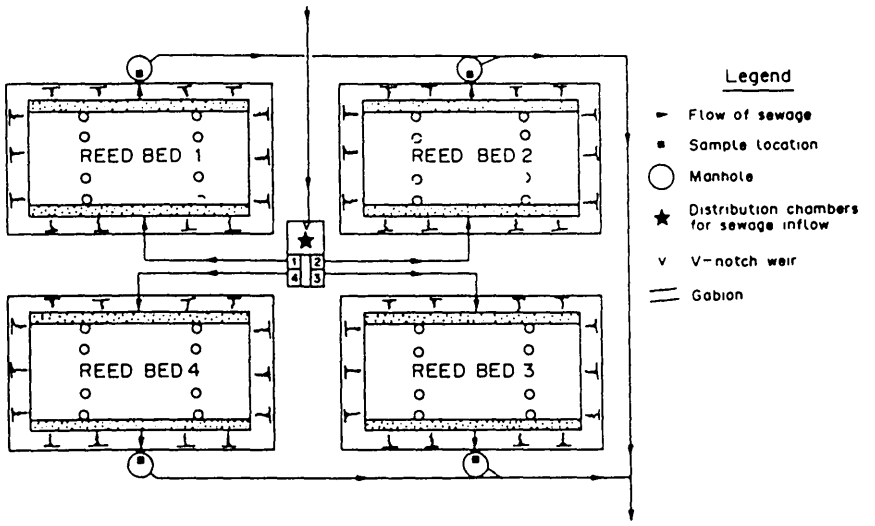


Figure 6.2: Plan of the Valleyfield reed bed system.

Under the contract with Fife Regional Council, from which the site was inherited, only two (Beds 1 and 3, Appendix 4) out of the four beds were allowed to be used for this investigation. Work on re-filling the two beds with shale commenced in January 1995. The beds were drained and the flow was blocked off in order to allow time for the material replacement. The existing material from the two beds was excavated down to within 0.01 m of the liner with extreme care not to cause any damage to the liner. Plant roots were separated from the excavated material using a muck fork and left for replanting. Shale was obtained from the same quarry (Cultshill, Ladybank) as the one used as a source for the laboratory and greenhouse experiments. The two beds were re-filled with 25 m^3 of material each, giving a pore space of approximately 7.5 m^3. Roots of *Phragmites australis* were planted to a depth of 0.15 m from the surface of bed 3, whilst bed 1 was retained unplanted to serve as control.

Water sampling started at the end of February 1995. From the very first sampling occasion, several problems occurred in connection with the flow distribution. The

10 - 15 days). The gabions were completely clogged with organic matter, resulting in uneven distribution of flow across the beds, which led to the occurrence of surface flows. There was also a major fault with the 'tipping trough' flow distribution system, because the bearings which were supposed to hold it in a fixed position on the main frame were missing. This prevented any control over the flow rates. It took the following month and a half for the tipping bucket to be repaired and fixed back onto the main frame. However, after only two weeks of proper functioning the bearings broke off and because of the lack of funding it was decided to make only a temporary repair of the flow chamber, and this had to be checked every week subsequently. Because of these problems, sampling was carried out only from June until September and no data on winter performance were collected. Nutrient concentrations and flow rates at the inlet and two outlets were monitored once a week during this three month period.

Daily visits were made to the site the following spring, in the period between 29/03 and 04/04/1996, to investigate hydraulic residence time and flow characteristics of the systems. Two bromide tracer tests were carried out: in the first one, sampling ports were installed at four locations along the length of each bed (0.5 m, 1.5 m, 2.5 m and 3.5 m from the inlet), and at three different depths (0.1 m, 0.2 m, and 0.35 m from the surface of the shale) (Figure 6.3) similarly to the greenhouse study (Chapter 4). A solution containing 20 g l^{-1} of Br^- (as KBr) was prepared and 25 l were added to each bed. The first set of samples was collected from each of the observation points (plus the outlet) one hour after the tracer pulse application, using 50 ml syringes. Monitoring of the tracer continued for 7 days, with samples taken once per day. In the second tracer test, the same amount of bromide (25 l of a solution containing 20 g l^{-1} of Br^-) was applied on the last day of measurements, and samples of wastewater taken at the outlets, every 10 minutes during one hour.

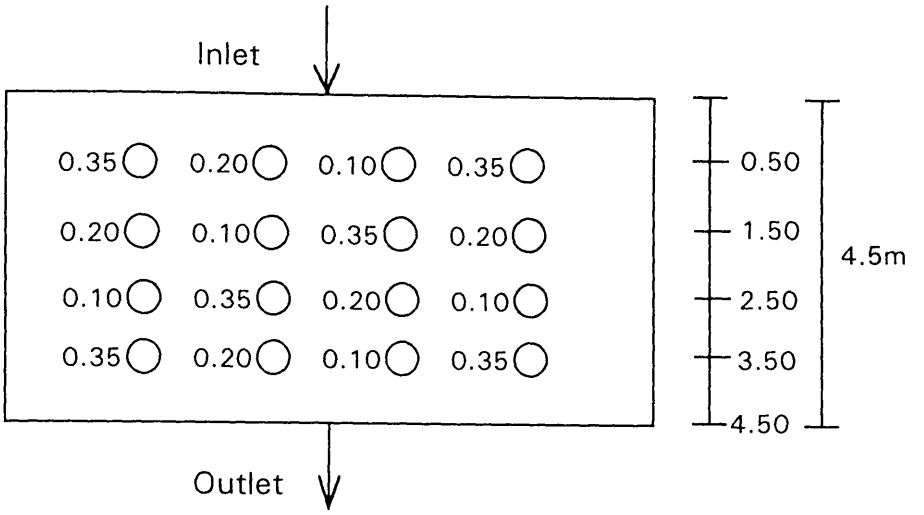


Figure 6.3: Aerial view of the tracer observation pints.

Bromide concentrations were determined using an ion-selective electrode (Adriano and Doner, 1982) (Appendix 3). It was also decided to monitor total phosphorus (TP), total nitrogen (TN), $H_2PO_4^-$ and NH_4^+ concentrations in order to check whether there was any difference in performance of the beds after the first winter season.

$H_2PO_4^-$ was determined using the standard ammonium molybdate method (DoE, 1980). NH_4^+ was measured using the method by Crooke and Simpson (1971) and NO_3^- by the method described by Best (1976) using a Chemlab Instruments Ltd continuous flow analyser.

Total phosphorus was determined according to a method by DoE (1980), in which organic P is converted into phosphate form during the digestion procedure with concentrated H_2SO_4. Total (Kjeldahl) nitrogen was determined using the slightly modified method by Rowell (1994) in which organic N in the sample is converted to NH_4^+ - N by digestion with concentrated H_2SO_4, and the NH_4^+ - N is determined from the amount of NH_3 liberated by distillation of the digest with the alkali.

Additional samples were taken for measurements of pH, redox potential (E_h) and temperature (t) in order to investigate the possible effects of these parameters on P and N removal from sewage. pH and E_h values were by standard techniques described by Rowell (1994), using a glass electrode, a reference electrode and a pH meter. Temperature was measured using a combined oxygen electrode and temperature recorder.

6.3. Results

6.3.1. Nutrient removal

Loading rates (plan surface area) and corresponding percentage removal rates (for the period June - September 1995) are presented in Figures 6.4 for phosphate and 6.5 for ammonium and nitrate. pH, E_h and temperature data are presented in Figure 6.6. Despite rather high input loading rates of phosphate (between 3 and 5 g m^{-2} day^{-1}, concentrations of 36 to 60 g PO_4 m^{-3}) the overall reduction was relatively high in planted beds (between 50 - 70%) while in unplanted beds it varied between 20 and 40 % (Figure 6.4). The reduction in ammonium occurred only during the first two weeks of sampling, and it was rather low in both the planted and unplanted beds (only 25 %). Moreover, in the remaining period of the investigation, ammonium concentrations were higher at the outlets than at the inlets with an increased removal (to 50% in both the planted and unplanted bed) occurring on only one sampling occasion on day 70 (Figure 6.5). Similarly to the greenhouse systems, nitrate inlet and consequently outlet concentrations were extremely low (between 0.2 and 0.6 g m^{-3}) with an increase to 2 g m^{-3} on one sampling occasion only (day 70). The removal rates varied between 75 and 25 %, decreasing to zero and then showing an increase of up to 25 % in August 1995 (days 40 and 55).

pH values were fairly stable throughout the period of investigation, ranging from 7 to 7.5, being slightly higher than in a green-house tanks, which could have affected the

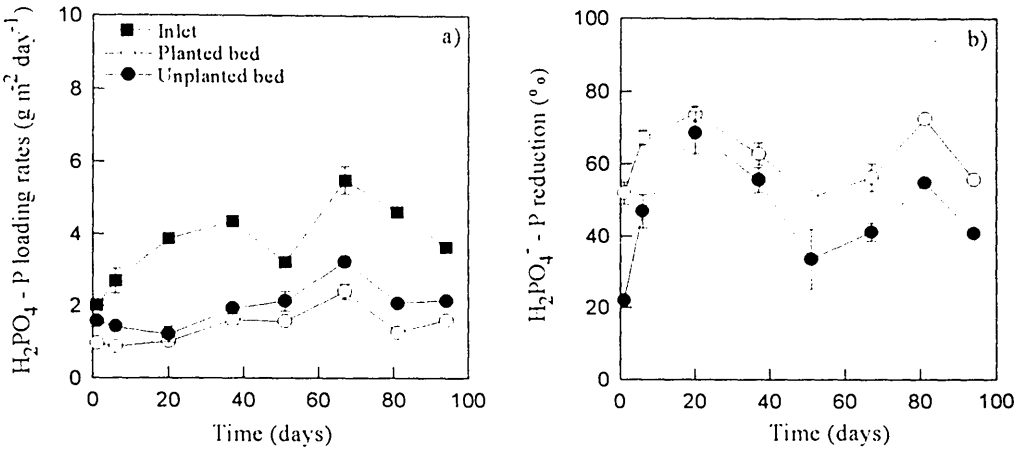


Figure 6.4: H_2PO_4- - P removal for the period June - September 1995. In b) open symbols represent removal of phosphate in the planted bed, solid symbols in the unplanted. Vertical bars denote standard deviation (SD).

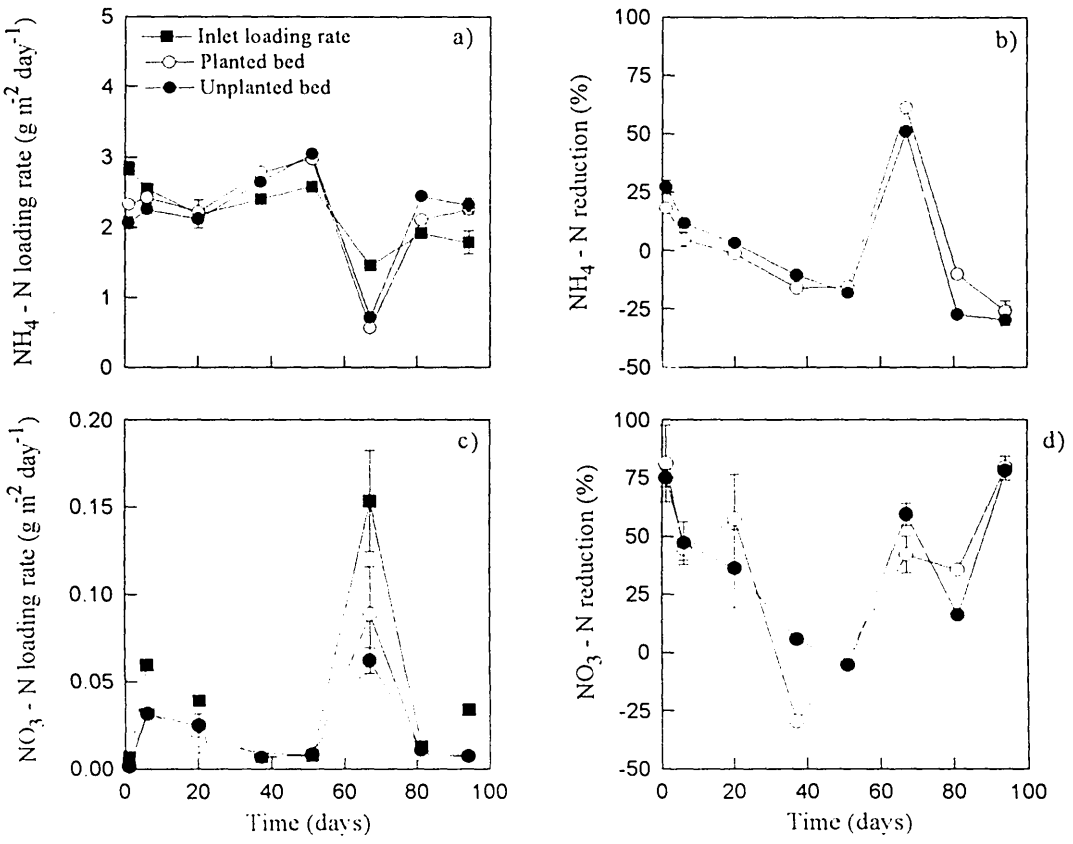


Figure 6.5: NH_4+ - N and NO_3^- - N removal for the period June - September 1995. In b) open symbols represent removal of phosphate in the planted bed, solid symbols in the unplanted. Vertical bars denote standard deviation (SD).

performance of the systems (see Chapter 1, Sections 1.7.4 and 1.7.5). E_h values of the

influent ranged from -50 to -25 mV, being lower than the effluent values which were between -25 and 0 mV. Temperatures were rather high during July and August (between 22 and 25 ^{o}C), while in September the temperature decreased to between 10 ^{o}C and 15 ^{o}C (Figure 6.6).

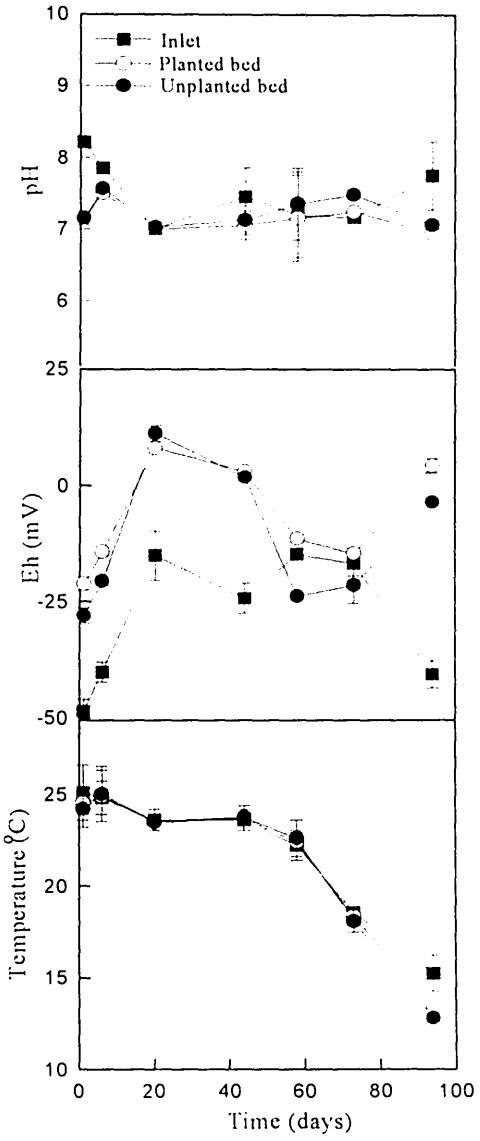


Figure 6.6: pH, E_h and temperature values for the period June - September 1996. Vertical bars denote standard deviation (sd).

As there were no replicate beds in the field, statistical analyses could only be performed to establish whether there was any significant difference in performance between the planted and unplanted bed. ANOVA analyses (one-way repeated measures) were performed, using SigmaStat statistical software (Kuo *et al.*, 1992).

The planted and unplanted bed were only statistically different with respect to P removal, pH and E_h.

Table 6.1: The effect of presence of *Phragmites* on H_2PO_4- - P, NH_4 - N, NO_3 - N, pH, E_h and temperature.

Parameter	Unplanted/planted BED_1 and BED_3
H_2PO_4-	$p < 0.02$
NH_4 - N	ns
NO_3 - N	ns
pH	$p < 0.05$
E_h	$p < 0.05$
t	ns

The results of TP, $H_2PO_4^-$ - P, TN and NH_4^+ - N analyses carried out in March 1996 are presented on Figures 6.7 and 6.8, below:

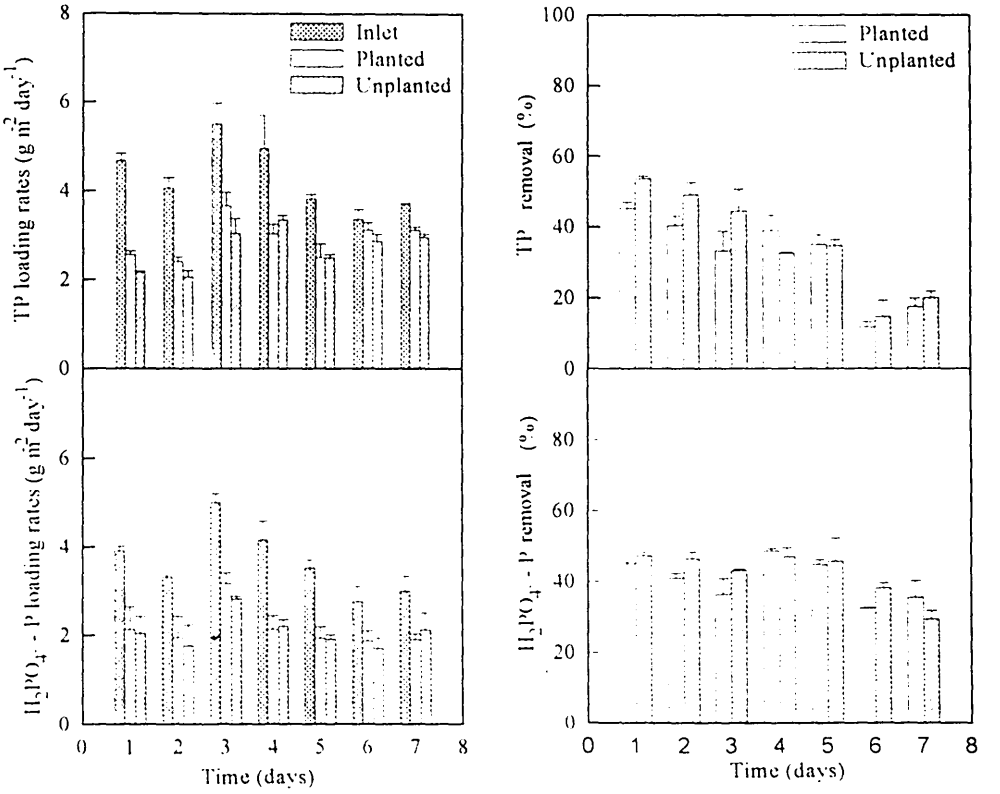


Figure 6.7: TP and $H_2PO_4^-$ - P removal for the period 29/03 - 04/04 1996. Vertical bars denote standard deviation (SD) ;n = 3.

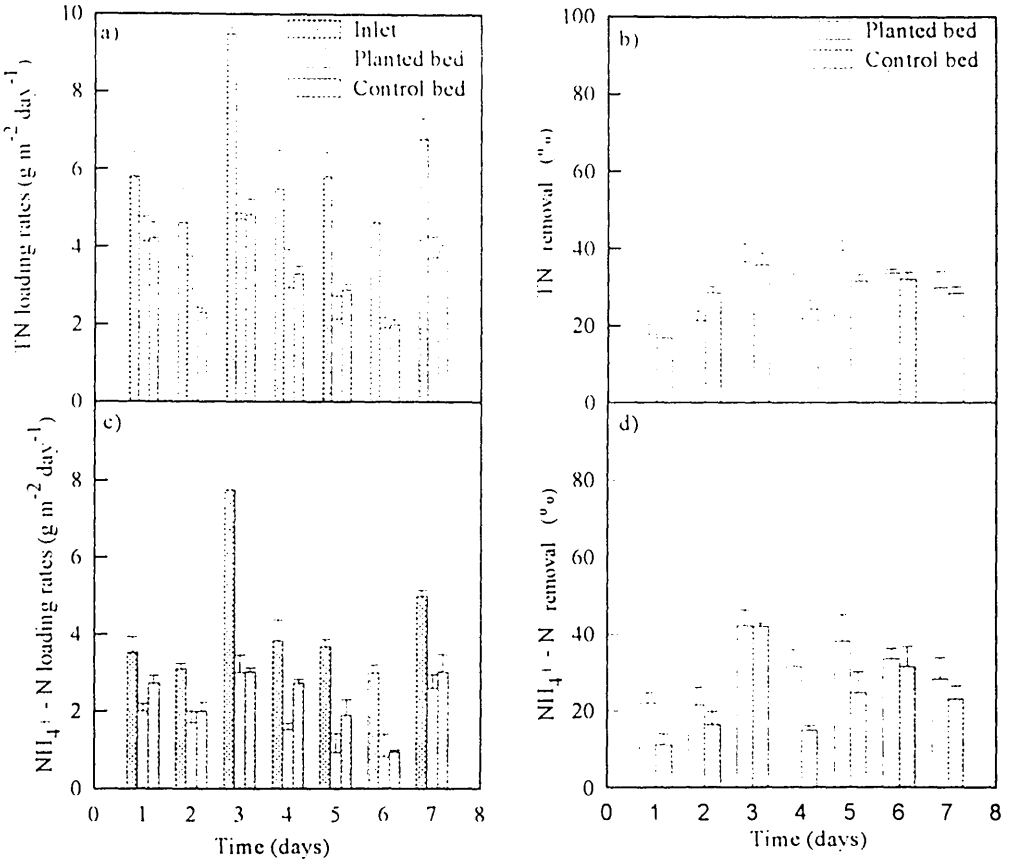


Figure 6.8: TN and NH_4+ - N and removal for the period 29/03 - 04/04 1996. Vertical bars denote standard deviation (SD).

Removal in both total phosphorus and phosphate (Figure 6.7 b and 6.7 d) was higher in the unplanted than in the planted bed, but this difference was not statistically significant. In addition, phosphate removal in both the unplanted and planted bed decreased by approximately 10 % and 15 - 30 %, respectively, when compared to the values from the previous summer (Figure 6.4). On the other hand, removal of ammonium in both the unplanted and planted bed increased by approximately 30 % - 40 % (Figure 6.8 d).

6.3.2. Hydraulic regime

The majority of wastewater travelled along the inlet and left-hand edge in both the unplanted and the planted bed. The results of the first tracer experiment revealed that only a small portion of the flow travelled through the beds, as only 16.7 % (unplanted) and 10.4 % (planted) of the bromide tracer was recovered. The mean

hydraulic residence time at the outlets (for this portion of the flow) was between 2.5 and 3 days (Figures 6.9 and 6.10).

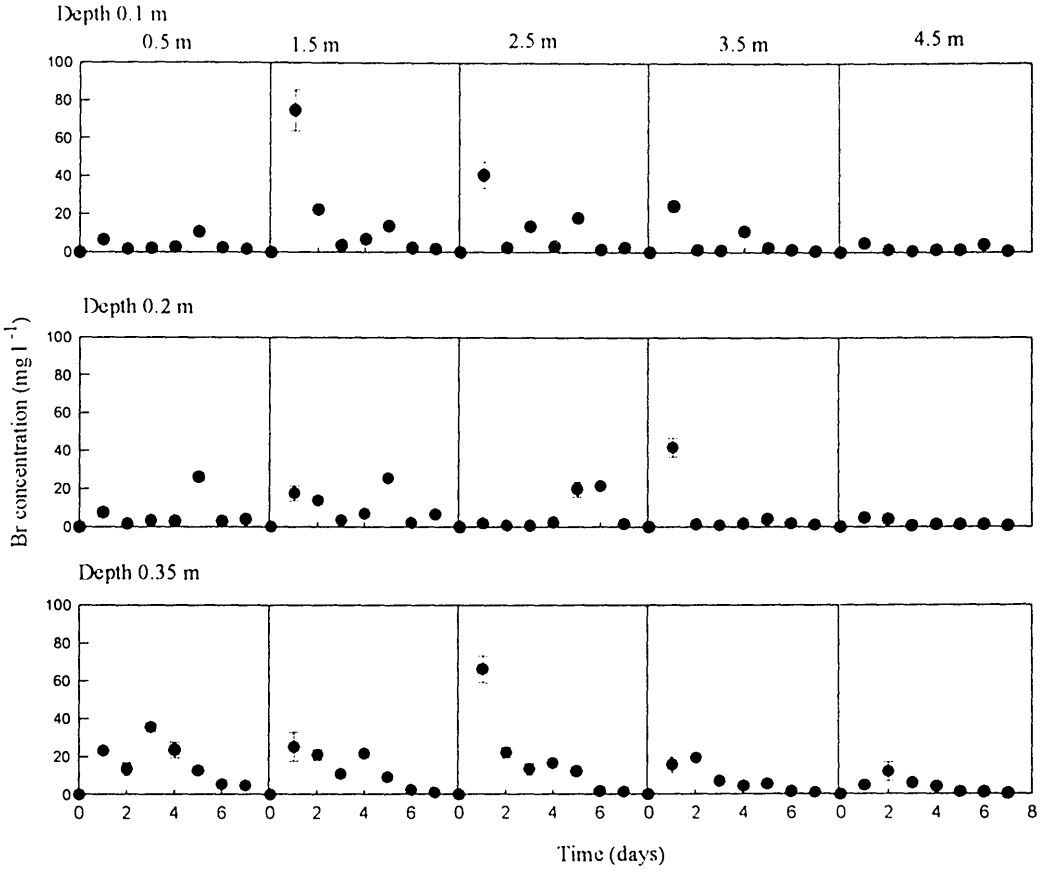


Figure 6.9: Bromide tracer concentration-time curves for 0.1, 0.2 and 0.35 m sampling depths at different positions along unplanted bed.

The second tracer experiment (29/03-04/04/1996), carried out on April 4th, 1996 showed that the majority of bromide applied passed through both the unplanted and planted bed in less than one hour (Figure 6.11 a and 6.11 b). The tracer curve of the unplanted bed is characterised by a sharp peak and a rapid arrival at the outlet point. Although the arrival peak of the planted bed was smaller, the hydraulic residence time of both the unplanted and planted bed was the same and amounted to approximately 35 minutes. The overall recovery of the bromide tracer was better than in the previous experiment, representing 94.5 % in the unplanted and 56.2 % in the planted bed.

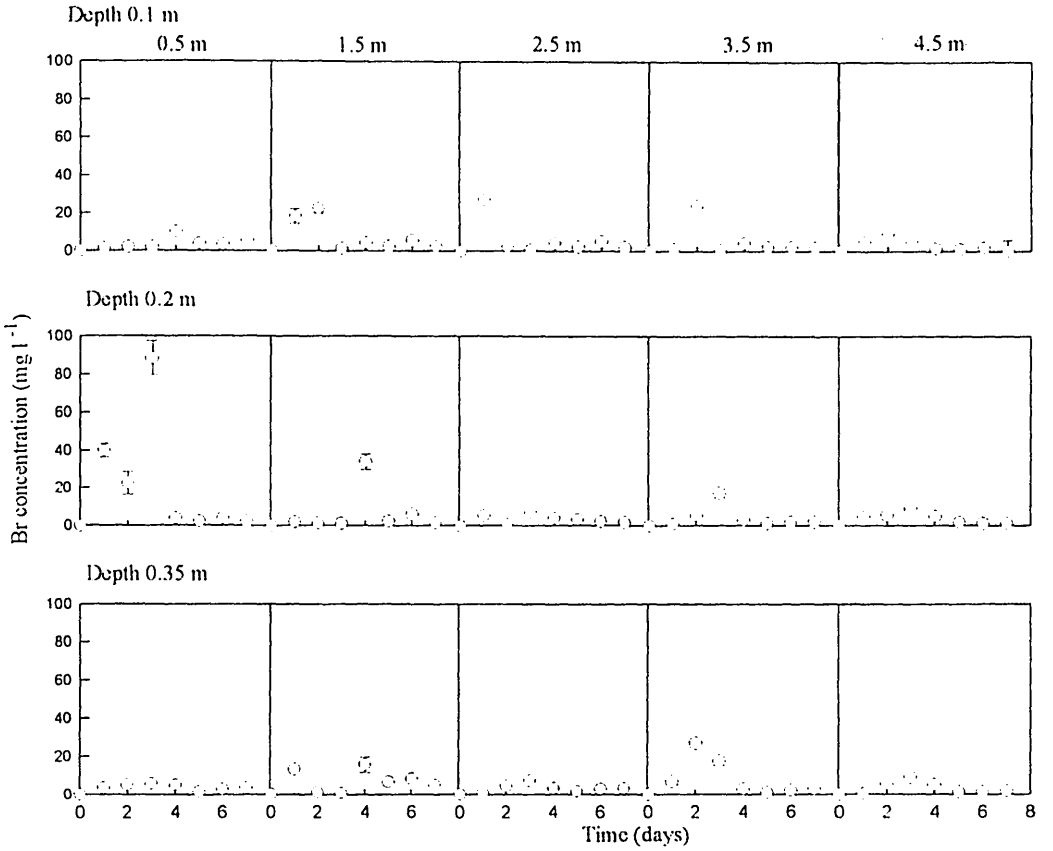


Figure 6.10: Bromide tracer concentration-time curves for 0.1, 0.2 and 0.35 m sampling depths at different positions along the planted bed.

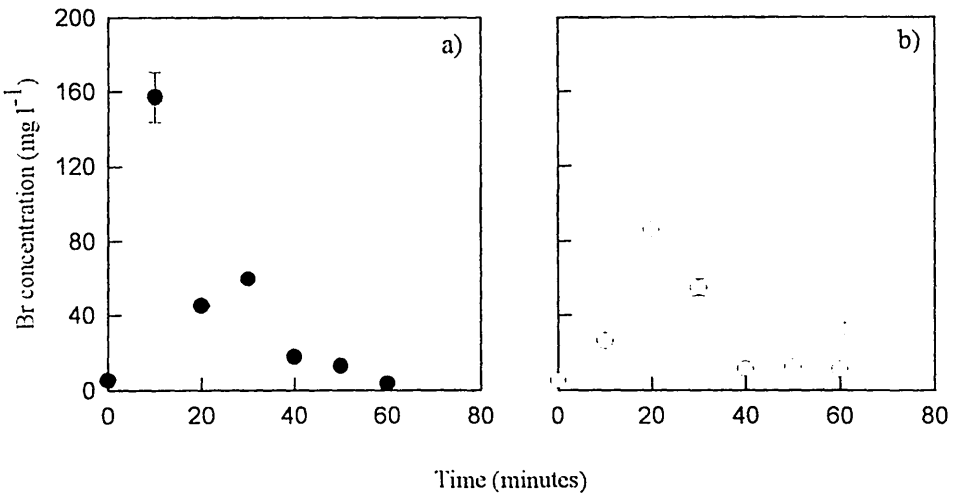


Figure 6.11: Bromide tracer concentration-time curves at the outlets of (a) the unplanted and (b) the planted bed.

6.4. Discussion

Although phosphate removal in planted beds was between 50 -75 % (Figure 6.4), the overall performance of the field systems was disappointing during the period June - August 1995, especially with regard to ammonium removal. This is believed to be caused by the poor hydraulic design of the systems. Fast surface flows, chanellization, short circuiting and occurrence of preferential flows were obvious from the very first visit to the site. The gabions were completely clogged and large areas of scum formed around the inlets of both beds. The same was observed in the remaining two beds (Plate 6.1 and 6.2).

Plate 6.1 The view of the surface and preferential flows over the Valleyfield constructed wetland system.

Plate 6.2: Another view of the surface and preferential flows over the Valleyfield constructed wetland system.

Ammonium and phosphate retention by wetlands are largely dependent on the sorption sites of the substrate (Richardson and Davis, 1987; Moshiri 1993; Sikora *et al.*, 1995). The poor performance of the Valleyfield systems could be attributed to the insufficient contact time between the sewage and shale caused by the hydraulic design. Low removal of nutrients is often associated with high input loading rates and short hydraulic retention times (Richardson and Nichols, 1987), which were the main hydraulic characteristics of the field system. In addition, the summer of 1995 was extremely dry and was one of the warmest of the century, resulting in no precipitation and therefore little possibility of dilution of sewage within the system. Another possible explanation could be an increase in mineralisation of N from bacterial cells, root material, plant exudates etc. The only increase in ammonium removal which occurred on day 70 in both beds, probably resulted from a 33 % decrease in inlet

loading, rather then improved overall nutrient cycling within the systems (Figure 6.5a).

Nitrate input and output loading rates were extremely low (below 0.05 g m^{-2} day^{-1}, except on one occasion) being typical of reduced environments (Figure 6.5 b). The fact that there was no significant difference in nitrate concentration in planted and unplanted bed indicates that plants contributed very little to the aeration of the system.

As overall phosphate and ammonium removal was strongly influenced by the hydraulic design of the system it was hard to draw conclusions about the effects of pH, E_h and temperature.

During sampling period in spring 1996 there was no significant difference observed between TP and $H_2PO_4^-$ values of the planted and unplanted bed (Figure 6.7), suggesting that plant uptake could only account for a very small fraction of the overall P removal. Moreover, while percentage removal of phosphate in the unplanted system remained in the same range of values (approximately 40 %) as the previous summer, indicating that the adsorptive capacity of shale functioned even under poor hydraulic design, the removal of the planted systems decreased by 25 % (falling from 70 to 45 %) (Figure 6.7 c and 6.7 d). This could be partially explained by the fact that plants still had not reached their maximum growth at the time of collecting data, as well as expected release of phosphate during winter, from the dead plant material (Wolstenholme and Bayes, 1990; Moshiri, 1993).

On the other hand, TN and NH_4^+ values were higher in the planted then unplanted bed (Figure 6.8). In addition, overall ammonium removal of both planted and unplanted system improved for approximately 30 % in spring 1996, when compared with the values from the previous summer (Figure 6.5 b). There could be few possible explanations for it. The oxygen availability within the system might have been improved via an internal pressurisation and convective throughflow mechanism driven by temperature gradients and water vapour pressure. The detailed discussion of these

mechanisms is given by Brix (1993). Secondly, the BOD might have increased during winter due to the accumulation of dead plant material, enhancing denitrification processes in the planted system (Green, 1997; Moshiri, 1993). This might have contributed to the improved ammonium removal rates in this bed. Lastly, precipitation during the winter months resulted in the dilution of the water in both the planted and unplanted system which might have improved the filtration and sedimentation processes leading to an overall improvement in the beds' performance with regard to ammonium removal.

The bromide tracer study carried out in spring of 1996 confirmed the short hydraulic retention times and heterogeneous flow mechanisms in both the unplanted and planted system. The negative effects which occurrence of preferential flows, surface channelling and short circuiting, as well as plant root development might have on the performance of the wetland systems are discussed in Chapter 5 (Section 5.4). Tracer test analyses carried out by Fife Regional Council in 1988 (one year after the system was established) revealed short retention times and problems with the hydraulic design. For example, it was pointed out that in a system with a single central inlet into a gabion, fluid distribution is limited (Fife Regional Council, 1988).

Due to the problems experienced with a double-acting tipping-trough (Section 6.2), in the present bromide tracer study, the inflow per bed was 2 - 4 times higher than designed for (approximately 10 - 14 m^3 d^{-1}, Section 6.2), which limited fluid distribution even more. Given the lack of a properly functioning pre-treatment unit, it is not surprising that fast surface flows occurred along the edges of the beds and that the majority of the tracer was recovered within less than an hour after application. In addition, preferential accumulation of solids in the inlet zone may have caused increased short-circuiting, causing parts of the beds to become dead-zones (Tanner and Sukias, 1995). This suggests that poor field performance was not caused by shale as a choice of bed medium, but by the problems with the wastewater distribution across the beds and hydraulic design.

6.5 Conclusions

The poor performance of field systems emphasises the importance of design in CWS application for wastewater treatment. Hydraulic considerations of the system differ with regard to the purpose of the treatment for which the CWS is built (Bavor, 1995; Kadlec, 1995). Despite a very low phosphate and ammonium removal achieved in the field systems, a lot of information had been gained regarding the design and the functioning of a CWS. For example, it became clear that if the combination of the screen as a pretreatment unit and gabions for the flow distribution is used, the CWS has little if any chance to produce a good quality effluent. The use of the screen as a pretreatment unit would also require frequent cleaning, which would increase the overall costs of maintenance of the system. Although quite simple in construction, the tipping - trough may not be the most appropriate system for the flow distribution. If used, the bearings should be built of stainless steel or other material resistant to corrosion. The system should be designed to cope with the maximum expected loading rates for the particular population equivalent, as the performance of the systems decreases significantly with increase in loading rates. Regarding the mechanisms of nutrient removal, it would be interesting to investigate the amount of nutrients which could be retained within sludge and sediments in the system (this was not measured in this project). In theory, the removal rate constants calculated for the greenhouse systems (Chapter 4) could be used to predict the performance of the full-scale systems. If it is assumed that the intended hydraulic loading rate (Section 6.2) was achieved and maintained, then 60 % removal would be expected for both P and N.

The investigation of the shale - based systems opens a new direction in the design of CWS as most of the systems built to date in the UK use gravel as a substrate. Shale proved to have better physical and chemical characteristics regarding P removal (Chapter 2), better purifying capability regarding P, N (chapters 3 and 4) and BOD (Elloriaga, 1996) and it is cheap and readily available in Scotland. However, because

of the problems with the hydraulic design of the Valleyfield systems, the application of shale as a substrate in full scale systems remains a subject for further investigation.

Chapter 7: Phosphate precipitation on shale and *Phragmites* root and rhizome surfaces

7.1. Introduction

The mechanisms involved in the precipitation of phosphate in wetland soils and sediments are discussed in Section 1.7.4.1. From the studies of P in soils and lake sediments, it is well established that phosphate is often deposited on the surface of relatively insoluble oxides and hydroxides of Fe and Al (Syers *et al*, 1973; Sawhney, 1977; Gambrell *et al*, 1990). This P is also called reductant soluble-P (RS-P) because strong reducing agents are required to dissolve the coating containing the P (Faulkner and Richardson, 1989).

The importance of this deposition process and its potential role in phosphate removal from wastewater has been reported by several authors (Stuanes, 1984; Faulkner and Richardson, 1989; Richardson and Craft, 1993; Cooke *et al*, 1993). The presence of P deposition on shale surfaces (packed in vertical columns), indicating the occurrence of precipitation reactions, was observed in an earlier experiment, using the X-ray fluorescence technique (Chapter 2). Therefore, initially, the idea was to investigate whether P deposition occurred on shale and plant surfaces taken from the CWS in the greenhouse and if so, to quantify the amounts of deposited coatings combining X-ray fluorescence and scanning electronic microscopy techniques. This information would help to calculate the total amount of P which could be retained within the shale substrate of the CWS (combined with the data on the P saturation point, Chapter 2 and P removal by the greenhouse CWS, Chapter 3) and predict the longevity of the shale based CW system.

Unfortunately, because of the detection limit of the analyser for P (concentrations of

at least 1000 mg kg^{-1} were required to be detectable), and difficulties in defining the boundary layers within the shale samples (how deep into the sample the electron beam penetrates, i.e. does it detect only minerals at the surface or below as well ?), it proved extremely difficult to quantify the amount of deposited P (D. James, pers. comm). Consequently, a decision was made to use a chemical extraction procedure instead. However, in their review of the application of this method in studies of P in sediments, Pettersson *et al* (1988) concluded that although it was established four decades ago (Chang and Jackson, 1957) it still has many limitations with regard to the order of extractions, method of P analyses and the type of sediment investigated. Therefore the results of this experiment provide only an approximate estimate of the quantities of P which might be coated on the shale and root surfaces.

7.2. Methods

7.2.1. X-ray fluorescence analysis

In November 1996 (the end of the experimental period in the greenhouse), individual samples of shale were taken from the points adjacent to the inlet and to the outlet end of both the planted and unplanted tanks in the greenhouse (in order to compare the difference between the two ends of the CWS). In addition, several *Phragmites* plants were excavated from the same areas of the planted tanks in order to examine the nature of the coatings on the root surfaces. The samples (roots and shale fragments) were placed on trays and left to dry for 48 h at constant temperature (21 ^{o}C). They were then cut into 20 - 40 mm sections and analysed using an energy-dispersive X-ray fluorescence analyser (EDAX Stereoscan 604, Cambridge, UK). This technique is based on bombarding the sample substance with the radiation from an X-ray tube. The chemical composition of the material is obtained by measuring the intensity of the radiation from the sample at different energies (Jones, 1990).

7.2.2. Chemical extraction

In the second part of the experiment, three different acids (ammonium acetate, 2 % citric acid and 0.1 M hydrochloric acid) were used in an attempt to separate chemically the extractable P from the shale surfaces. Because there is no established method for this kind of investigation for shale, it had been decided to make four different trials: three separate aliquots of 50 g of shale were equilibrated with 150 ml (weight to solution ratio 1:3) of ammonium acetate and 150 ml of 2 % citric acid, respectively, for 24 h by continuous shaking on a rotating shaker at constant temperature (21^{o}C), to examine the difference in the quantities of extractable P when extractants of different strengths were used. In addition, 0.1 M HCl was tested on a further 50 g of shale (three replicates), with the time of equilibration decreased to 6 h. This was done in order to avoid the possibility of attack on the areas below the shale surface, which might have happened because of the greater strength of the HCl (Dr Tony Edwards, pers. comm). In the last trial, further shale samples (three of each) were again treated with 2 % citric acid, but the time of equilibration was extended to 32 h. In all four cases, the quantities of deposited P dissolved by the reagents were determined using an inductively coupled argon plasma spectrometer (ICP) (DoE, 1986).

7.3. Results

7.3. 1. XRF analysis

Similarly to the earlier experiment (Chapter 2), changes in colour were observed on the surfaces of all shale samples, regardless of the location within the tank, as well as on the plant roots. The X - ray spectra of the coatings on untreated, unplanted and planted shale samples as well as the root surface (two of each sample) are presented in Figure 7.1. The X-ray count rate is directly proportional to the chemical concentration (Brindley and Brown, 1980). The spectra of the untreated shale and samples taken from the planted tank had a similar shape, the important difference being that unlike the untreated sample, a small P peak was detected on the shale

samples taken from the planted tank (Figure 7.1a and 7.1c). In both cases, the most prominent peak was Si, followed by Al and Fe. The shale samples from the unplanted tank had a very different shape (Figure 7.1b) with a 6 - fold higher Fe peak, and with Si and Al peaks reduced to one sixth and one quarter, respectively, of their former size (Figure 7.1b), when compared with the untreated shale samples and those taken from the planted tank. Spectra of the *Phragmites* root surfaces confirmed the potential for metal deposition, with Al, Si, Fe and K peaks being similar to the untreated shale and shale samples taken from the planted tanks, and the P peak being similar to the one from the samples from the unplanted tank (Figure 1d). In addition, the Ca peak was twice as large when compared with other samples and S, Cl, Cu and Zn peaks became detectable.

7.3.2. Chemical extraction

The results of chemical extractions showed that in both the unplanted and planted tanks and in all 4 trials, the quantities of extractable P were higher at the inlet end than at the outlet end of the CWS (Figure 7.2). In the unplanted tank, the P extracted from the sample taken at the inlet end was on average 3 times higher than at the outlet end (0.1 g kg^{-1} and 0.03 g kg^{-1}), while in the planted tank it was eight times higher (0.08 g kg^{-1} and 0.01 g kg^{-1}). The quantities of P extracted are presented in Table 7.1. These data show that the highest amounts of P were extracted by 2 % citric acid. The extended period of equilibration of 8 h (from 24 to 32 h) increased the quantities of extractable P by a factor of 1.6 - 3.

The amounts of P on the shale surfaces at the inlet ends of the unplanted and planted tanks, as estimated by the extractions, should be treated with caution, due to the limitations of the technique used. However, an attempt has been made to estimate the amount of P which could be retained within the CWS due to the precipitation reactions (based on the obtained values). The total input of P over the whole period of investigation (309 days) was 174.4 g P, the total output in the unplanted tanks was 5.4 g and in the planted ones 0.8 g. Cumulative P adsorbtion for greenhouse tanks

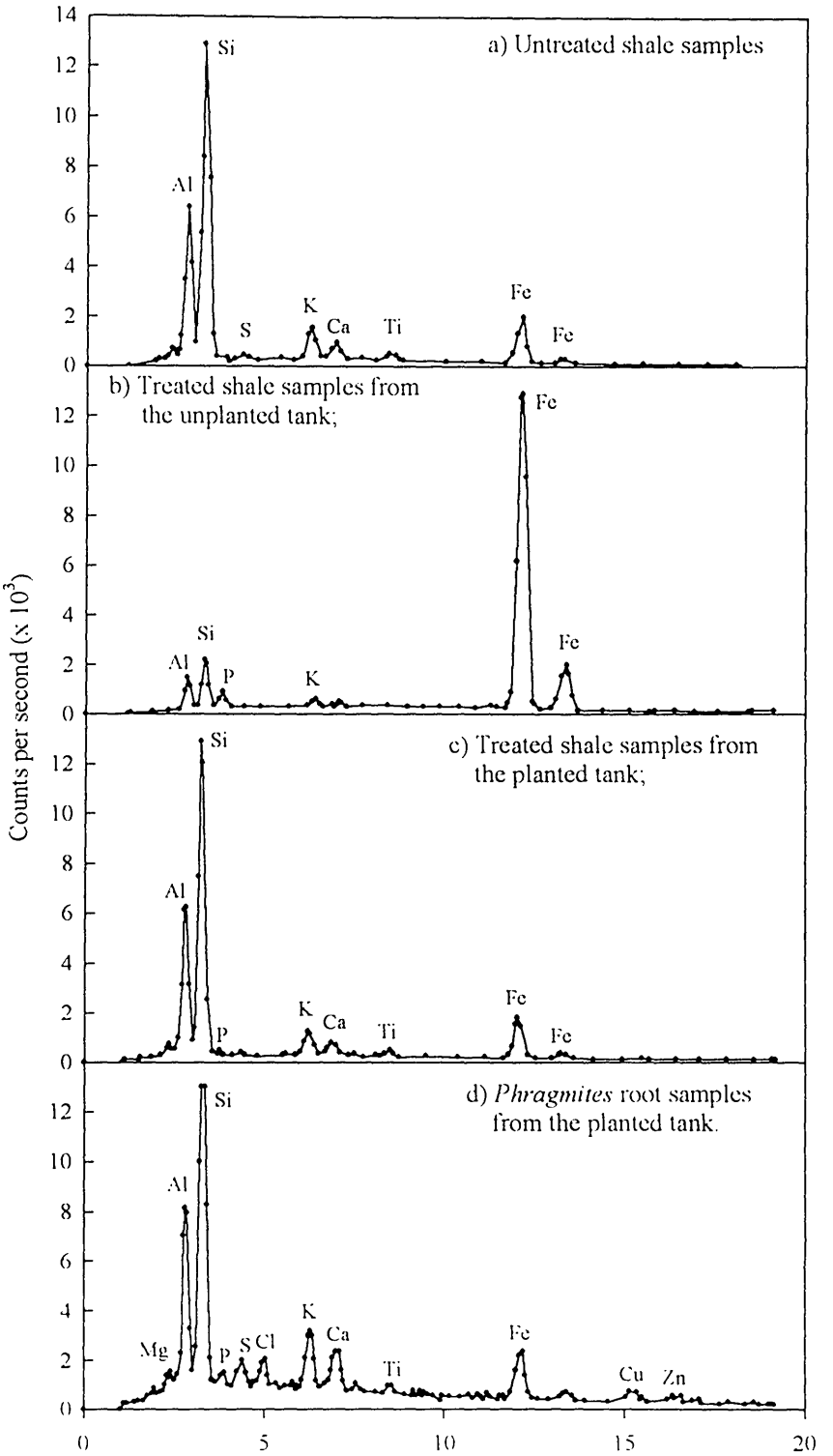


Figure 7.1: X-ray fluorescence spectra from shale and *Phragmites* surfaces.

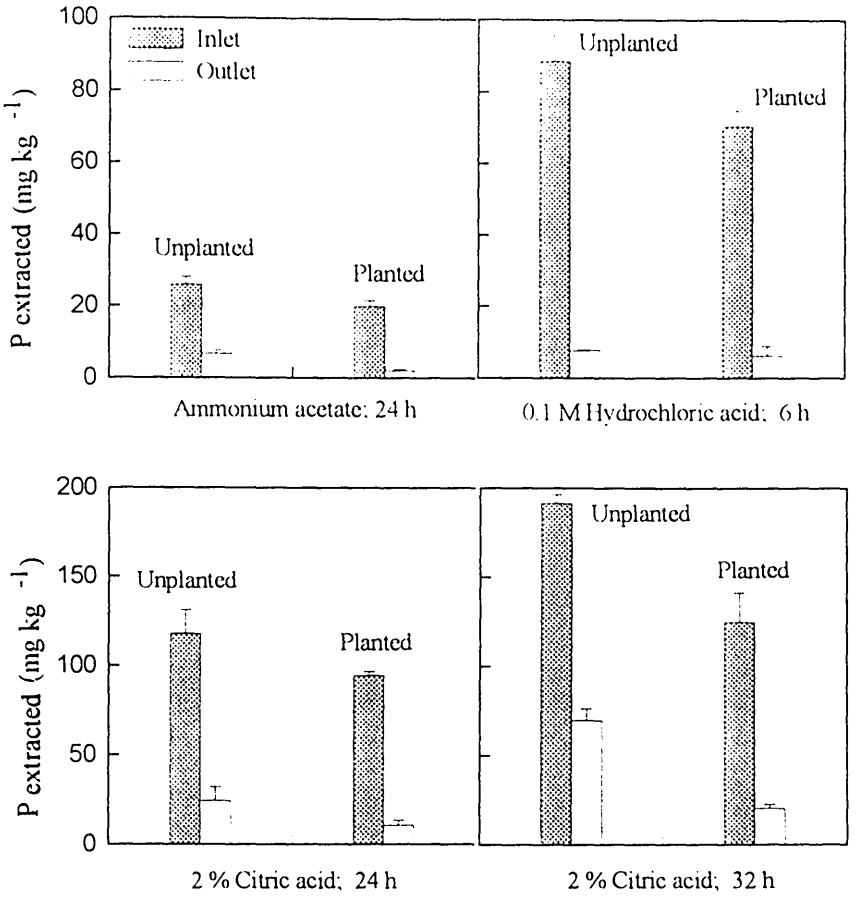


Figure 7.2: P extracted from shale surfaces by different reagents. Three replicate samples of shale taken from points adjacent to the inlet and to the outlet end, respectively of both the planted and unplanted tanks in the greenhouse (in order to compare the difference between the two ends of the CWS). Each column is the mean of 3 replicate measurements. Vertical bars denote standard deviation (SD).

(Chapter 4) showed that in the unplanted tanks, the total P uptake was 0.85 g P kg^{-1} while in the unplanted it was not significantly different, 0.87 g P kg^{-1}. If the values of P precipitation from the inlets and the outlets of both the unplanted and planted tanks are averaged for the whole CWS, the quantity of deposited P on the shale surfaces for unplanted and planted tank are 0.07 and 0.04 g P kg^{-1} which amounts to only 7.8 and 5 %, respectively, of the P removed from solution. This suggests that the extraction method is not very efficient and that sequential extraction with increasingly powerful reagents would be a better approach.

Table 7.1: Phosphate extraction (mg kg^{-1}) from shale surfaces treated by different reagents

Source of shale	P extracted (mg kg^{-1})							
	NH_4 acetate, 24 h		2% citric acid, 24 h		2% citric acid, 32 h		0.1 M HCl, 6 h	
	Unplanted	Planted	Unplanted	Planted	Unplanted	Planted	Unplanted	Planted
Untreated material	24.2 ± 5.5	24.2 ± 5.5	168.0 ± 3.8	168.0 ± 3.8	293.6 ± 6.3	293.6 ± 6.3	66.3 ± 5.2	66.3 ± 5.2
Tank inlet	50.1 ± 3.4	43.9 ± 3.7	285.9 ± 9.2	262.7 ± 5.9	485.2 ± 4.8	397.6 ± 29.8	154.8 ± 19.4	136.8 ± 9.6
Difference	25.9 ± 2.1	19.7 ± 1.7	117.9 ± 12.9	94.7 ± 2.1	191.6 ± 11.1	125.1 ± 16.1	88.5 ± 14.1	70.5 ± 4.3
Tank outlet	30.8 ± 4.6	28.0 ± 5.0	192.6 ± 3.7	178.5 ± 6.6	363.2 ± 23.1	314.0 ± 4.0	73.9 ± 5.1	72.5 ± 2.6
Difference	6.6 ± 0.9	3.9 ± 0.5	24.6 ± 4.6	10.5 ± 2.8	69.6 ± 6.7	20.3 ± 2.3	7.6 ± 0.1	6.2 ± 0.6

* Each number represents mean value of three replicates ± standard deviation.

7.4. Discussion

The results of these experiments provide only preliminary information about phosphate precipitation reactions on shale and plant root surfaces. Nevertheless, three important facts were revealed:

i) all the extractants removed significantly more P from the shale in the tanks than from untreated shale, showing conclusively that P had been deposited as a result of the use of the shale in the CWS;

ii) all the extraction experiments showed clearly that the deposition was heavily concentrated near the inlet - the ratios of additional $P_{extr.\ (inlet)}$/ $P_{extr.\ (outlet)}$ varied from 11.6 : 1 to 2.75 :1 in unplanted and from 11.4 : 1 to 5.0 : 1 in planted tanks.

iii) the deposited P was predominantly in relatively unavailable forms - the quantity removed by NH_4 acetate (i.e. the readily exchangeable phosphate ions) was much less than that which could be dissolved by 2 % citric acid or 0.1 M HCl (Table 7.1).

The fact that P depositions were higher at the inlet than at the outlet end in both the unplanted and planted CWS is in accordance with other studies, which showed that a large proportion of wastewater pollutants in general tend to accumulate within the limited area of the inlet zone (Reed, 1992; Davis and Cottingham, 1993; Bavor, 1995; Wood, 1995). Patrick and Khalid (1974) found that under anaerobic conditions, soils sorbed P from solutions containing high concentrations of soluble P. As P concentrations in wastewater were higher at the inlet end than at the outlet (Chapter 3) it was expected that adsorption in combination with settling would result in higher P depositions at the inlet end of a CWS. This turned out to be the case. Similarly, the higher P concentrations in the wastewater in unplanted tanks than in planted tanks explains the former's higher level of P deposition in both inlet and outlet. That the difference between the inlet end and the outlet end in the planted tanks was higher (8 fold) than in the unplanted tank (4-fold) could be attributed to plant uptake combined with the increased available surface area for precipitation due to the presence of plant roots as the wastewater travels through the system.

The most stable Al - P, Fe - P and Ca - P mineral compounds (in soils) are variscite, strengite and fluorapatite, respectively (Talibudeen, 1981). Lindsay (1979) pointed out that upon flooding, P in soils may be transformed from one mineral form to another. For example, as redox potential decreases to the levels where Fe^{3+} reduction occurs, magnetite (Fe_3O_4) becomes more stable than soil $Fe(OH)_3$, the solid phase iron which controls Fe^{3+} activity in the soil. As a result, Fe^{3+} activity in the solution drops, causing strengite to dissolve, thereby supporting higher P concentrations which maintain the solubility product constant. With the further decrease of redox potential, the point might be reached where, theoretically, vivianite, an Fe-P mineral, becomes the most stable P-mineral. According to Lindsey (1979), variscite (Al-P) and strengite (Fe-P) are frequently transformed to vivianite [$Fe_3(PO_4)_2$ $8H_2O$] in flooded soil systems.

Results from the X-ray spectra analyses showed that, in the unplanted tank, there was a large increase in Fe deposition and a small peak of P (which was absent for untreated shale). The reduced peaks of Al and Si may be an artefact, due to the Fe and P deposition, because the shale has a high aluminosilicate content throughout and this would have not been removed. In the planted shale tank no such Fe deposition was observed and therefore there was no deposit to obscure the Al and Si content. In addition, the P peak was smaller in the planted than in the unplanted tank (this difference could be due to the plant's uptake). The X-ray spectra of the root surface confirmed the potential of *Phragmites* for metals retention as indicated in Chapter 3 (Section 3.3.4). This is also in agreement with Peverly *et al.* (1995), who investigated trace metal adsorption by *Phragmites* and suggested that metal precipitation occurred due to the presence of a thin oxidized layer on the surface of the roots, described by Brix 1994b). However, these differences in X-ray patterns between unplanted and planted tanks are surprising, in view of fact that the chemical extraction results show only a relatively small difference between unplanted and planted tanks. Additional analysis, possibly using XRFs combined with scanning electron microscopy, are necessary to be able to identify mineral transformations which occur on the shale and plant surfaces.

7.5. Conclusions

Although it was not possible to make a quantitative estimate of the surface deposits, data from the X-ray spectra analyses were important for several reasons: firstly, they confirmed previous findings that P does precipitate on shale surfaces (Chapter 2, Section 2.3.3); secondly, they provided information on the range of elements which may occur on the shale surfaces; thirdly, they confirmed the potential of *Phragmites* for metal uptake. The results also support the theory on phosphate accumulation within the inlet zone of a CWS (and are in accordance with the findings from Chapter 4). They also open a new direction for further investigations of P retention mechanisms. For example, it would be interesting to make sequential extractions to fractionate substrate phosphorus and quantify aluminium-bound P, iron-bound P, calcium-bound P, reductant soluble P and organic P. This investigation could be coupled with scanning electron microscopy and X-ray fluorescence analysis to provide fuller information on the nature of P depositions which occur on the shale and plant surfaces.

Chapter 8: Discussion and conclusions

8.1. UK needs for wastewater treatment and a role for CWS

The UK water industry has a record of service and expertise in providing relatively densely populated islands with wholesome water and sewage purification. The responsibility for water management in England and Wales relies at present on ten water and sewerage companies and 21 water supply companies. In Scotland, the organisation of the water industry and water-conservation practices has been different from those of England and Wales, mainly for historical reasons and partially due to the greater availability of water in Scotland (Adeloye *et al*, 1996). One of the consequences of this is that development of CWS technology for wastewater treatment has progressed faster in England than in Scotland, although the largest CWS that had been built so far in the UK (design population 12,000 p.e.) is situated in Scotland (Rawlinson, 1996).

In November 1994, legislation was passed to create publicly owned water authorities. Since then, the water authorities have assumed the ownership of all the existing water and sewerage assets in Scotland, maintain them and take responsibility for their operation. Also in 1994, legislation was introduced (HMSO, 1994) to form a Scottish Environmental Protection Agency (SEPA), which started its activities in April 1996. One of SEPA's primary objectives is the promotion of the cleanliness of rivers, other inland waters and Scottish tidal waters, and the conservation - so far as practicable - of the water resources of Scotland (Hills, 1995; SEPA, 1995). Currently, in Scotland, over 90% of the population is served by a public sewage collection and treatment system. Under-investment in infrastructure has allowed sewage to become the most important factor causing poor water quality. For example, according to SEPA (1995), it is estimated that £500 million will be required within the Forth catchment by 2005 to achieve the necessary improvements in environmental quality. The allocation of finance will determine the rate at which this programme is implemented. An adequate

level of spending is essential if public expectations are to be met and the country's obligations under European Community law fulfilled (SEPA, 1995).

It is well known that statutory powers provide the means of enforcing remedial action to reduce many pollution risks. However, the power provided by current legislation is limited. For example, the EC Urban Waste Water Directive (UWWD) was proposed back in 1991 and sets stringent new criteria for sewage effluents discharged to surface and coastal waters, depending on both the sizes of sewage treatment works and the sensitivity of the receiving water. As such, this Directive potentially has a special importance in the area of waste water purification, as it represents the first attempt to deal directly with nutrient enrichment by sewage effluent (Wilson *et al*, 1996). However, it has still (in 1998) not been adopted (Section 1.1), and the selection of sites for designation as sensitive areas has been left to member states. In the UK, for example, this led to controversy and disagreement between the Government's assessment and relevant bodies such as English Nature (EN) and former National River Authorities (NRA) which deal with the conservation of freshwater 'Sites of Special Scientific Interest' (SSSIs) which are subject to eutrophication. Moreover, it resulted in insufficient development of policy and legislation in the area of nutrient enrichment, and despite currently being a water-quality issue, nutrient levels are not subject to consent limits (Wilson *et al*, 1996). Therefore, it is not surprising that phosphate removal has not been studied in UK CWS to any great degree and that the application of CWS for ammonium removal has only started to expand recently (Cooper and Green, 1995; Cooper *et al*, 1996). The influence of planning authorities is especially important, for example because of the potential implications of land-use change on water quality. SEPA (1995) stated that the strategic planning should encourage land zoning and planning policies which promote sustainability and which are complementary to water quality objectives. In addition, it was further stated that the liaison between the planning and drainage authorities should ensure that development does not exceed sewer capacity. The parallel development of drainage infrastructure with other development is a critical strategic principle necessary to protect the environment (SEPA, 1995). However, in their **State of the Environment**

Report 1996, SEPA pointed out that '*inadequate or overloaded sewage treatment facilities continue to cause concern in specific locations around the country. The solution in most cases would be thorough investment of resources to provide or upgrade existing sewage treatment facilities*'.

As was pointed out in Sections 1.1 and 1.2, historically, sewage collected from sources near the coast used to be discharged, after screening, grit removal and primary treatment only, through a long pipeline into sea areas of high natural dispersion. By using the natural purification capacity of the sea, water suppliers created the most economic solution for the customers. However, by the turn of the century, the expected passing into UK law of the UWWD should ensure that secondary treatment will be introduced for discharges from specified population numbers to estuaries or coastal waters (Section 1.1, Table 1.1). The treated effluent will have to be of a high enough quality to allow safe discharge to a nearby watercourse. As pointed out in Section 1.1, the quality of any discharge is measured in terms of the demand that it makes for oxygen from the watercourse and its lack of suspended solids, and the amounts of ammonia and other poisonous substances present, all of which are critical to the well-being of river life (Hills, 1995; SEPA, 1995). In designated areas, secondary treatment of sewage and, in sensitive areas in particular, the removal of phosphorus and nitrogen will be required. By being both environmentally sustainable and economically viable, alternative wastewater treatment technologies might provide the most appropriate solution for meeting these objectives.

8.2. CWS technology

The advantages and disadvantages of CWS technology were outlined in Sections 1.7.6 and 1.7.7. Although CWS are attractive because of the low costs of construction and simplicity of operation and maintenance procedures, long-term management of these systems will require thorough understanding both of their

efficiency in removing waste constituents and of the physical, chemical and biological factors that affect these processes.

8.2.1. Testing of new and cheap materials

The earlier chapters demonstrate the importance of the substrate in the immobilisation of phosphate in constructed wetland systems. In their evaluation of the first ten years of experience with CWS in UK, Cooper and Green (1995) stated that almost all systems constructed since 1986/7 use gravel as a substrate. In the same study they pointed out that, although the systems have performed satisfactorily, phosphate removal had not been noted to any great degree. Therefore this thesis addressed this problem; an investigation has been carried out to select a substrate with the greatest potential for P removal, and in view of the fact that the substrate represents a major cost item in design of a subsurface flow CWS, due to transportation costs and labour involved in handling and spreading (Steiner and Freeman,1989), an effort was made to find a material that was both cheap and locally available, as well as efficient in P removal. As a result of the work described in Chapter 2 it is concluded that shale has many of the necessary properties and is the optimal substrate of the seven investigated.

Moreover, shale is widely available, forming 60 % of the world sediments (Potter *et al*, 1980). Thick beds of mudstone and shale form predominantly in aqueous environments and they represent a characteristic feature of river floodbasins, lakes, estuaries, continental shelves and ocean basins. They are also found in many of the formations of the Coal Measures (Potter *et al*, 1980; Ridgway, 1982). In Great Britain, shale deposits occur over wide areas representing practically all geological periods. Since 1895, almost 1,600 million tonnes of common clay and shale have been dug in the United Kingdom and annual production increased from approximately 10 to almost 38 million tonnes in 1968. Despite the fact that the output had fallen since then, the annual production was still over 25 million tonnes in 1978. Although the output of clay and shale was overtaken by those of limestone, sand and gravel and

indigenous rock in the early 1980s, the statistical data relating to the production, consumption and trade of shale revealed that clay and shale remained the basis of an industry with sales of over £300 million per year in 1982 (Ridgway, 1982). Shale was mainly used for building and engineering brick, floor and roofing tiles and agricultural field drains (Ridgway, 1982). Since then the industry has been in decline, leaving behind millions of tonnes in waste heaps (R.B. Speirs, pers. comm.). The use of this shale is therefore highly desirable, and may contribute to landscape rehabilitation.

8.2.2. Efficiency of nutrient removal in a small-scale system

Both unplanted and planted small-scale CWS showed an extremely high efficiency and achieved virtually a complete P removal (98 % of removal in the unplanted tanks and 99 % in the planted tanks). This remained true even when the influent concentration rates were increased from 40 to 120 g m^{-3}, i.e. 0.8 to 2.4 g P m^{-2} day^{-1} (Section 3.3.1). These results are particularly significant as they showed a higher efficiency of P removal than reported in other studies (Richardson and Davis, 1987; Faulkner and Richardson, 1989; Moshiri, 1993; Bavor, 1995), where the CWS performances ranged between 10 and 90 %, depending on the strength of wastewater entering the system, the physical and chemical characteristics of the substrate, and design and loading rates (Brix, 1993; Geller, 1997). For example, Brix and Schierup (1989) investigated the efficacy of 25 CWS in Denmark (with an average age of 4 years) and concluded that removal efficiency was poor (20 - 40 %). Kadlec and Knight (1996) reported that the three-cell, gravel-based CWS demonstration project in Benton, Kentucky, which was monitored over a period of 19 months in 1988/1989, removed only 7 - 19 % of the incoming total P, which entered at the moderate influent concentration of *circa* 5 mg l^{-1}. They also reviewed the data on the performance of the seven CWS in Richmond, New South Wales, Australia, which were monitored from June 1984 until May 1986, and stated that systems removed only 12 - 21 % of the influent P, which entered at a concentration of 9 mg l^{-1}. On the other hand, Maehlum *et al* (1995) reported P removal from multistage systems which had been installed in Norway, using especially manufactured material LECA as a substrate, to

be as high as > 95 %, which is the highest removal efficiency reported in the literature to date. In the present study, the pilot-scale shale based CWS were fed at the annual rate of approximately 300 g m^{-2} y^{-1} and were still able to remove 98 and 99 % after 11 months of monitoring. The fact that CWS remained highly effective even when the influent concentrations were increased three-fold suggests a flexibility of the shale based system to adapt to a range of concentrations (Haberl *et al*, 1995).

A monitoring of the performance of the field systems, during the 3-month period June-September 1995, further confirmed the efficacy of the shale as a CWS substrate. Although the input loading rates of P in the field systems were extremely high (between 3 and 5 g m^{-2} day^{-1}, equivalent to concentrations of 36 - 60 g m^{-3}), the overall reduction in the planted beds was relatively high (between 50 and 70%) while in the unplanted bed it varied between 20 and 40% (Figure 6.4, Chapter 6). The second investigation of the field system's performance, carried out for one week, for the period 29 March-4 April 1996 revealed the deterioration of the P removal performance (Figure 6.7, Chapter 6). However, as pointed out in Section 6.4 (Chapter 6) the field systems suffered from poor hydraulic design (preferential flows, surface channelling, clogging of the substrate) and therefore it is not surprising that they did not achieve better performance.

The small scale shale-based systems also demonstrated a high efficiency for ammonium (NH_4^+-N) removal. Although in the unplanted tanks NH_4^+-N removal varied between 40 and 75%, ammonium was completely removed in the planted tanks. Similarly to P removal, NH_4^+-N removal in CWS is highly variable and depends on the type and composition of the wastewater entering the system, the influent loading rates and physical and chemical characteristics of the substrate used (Brix, 1993; Cooper *et al*, 1996). The efficiency of 97-99 % achieved in the present study is higher than in many other subsurface flow systems described in the literature. For example, Scierup *et al* (1990) reviewed the performance of 71 mainly soil-based Danish CWS employing horizontal flow, and found that the average efficiency of

NH_4^+-N removal was 34%. Findlater *et al* (1990) reported that the efficiency of removal of NH_4^+-N from 43 UK CWS (which mainly used soil or coarse gravel as a media) was rather low, approximately 15% on average, with a slightly better performance observed in soil-based systems. Green and Upton (1995) reported the performance of several CWS, established by Severn Trent Water, UK, for treating secondary and tertiary wastewaters. The systems at Wetwood, Leeds, England were constructed in 1992 as three terraced gravel-filled beds which, after one year of operation, achieved only 29% removal of NH_4^+-N, while the other system, at Middleton, England, removed 32 %. Vymazal (1995) reviewed the performance of seven CWS in the Czech Republic, using sand, gravel and their mixtures as substrates, with particle sizes from 0 to 60 mm, and reported removal rates of 31%. In their overview on the performance of CWS in Europe, Haberl *et al* (1995) stated that the average removal of NH_4^+-N, in 268 European systems investigated, was approximately 30% and therefore the efficiency of the systems was not satisfactory. Wood (1995) reported that, for 300 North American wetland systems ranging in size from 40 m^2 to 10^4 m^2, removal rates were on average 44%, while Kadlec and Knight (1996) reported that NH_4^+-N removal in seven pilot-scale CWS in Richmond, New South Wales, Australia averaged 50 %.

In the current study, poor NH_4^+-N removal was also observed in the field systems, which were monitored during the summer of 1995. The removal of NH_4^+-N occurred only during the first two weeks of sampling and it was rather low in both the planted and unplanted system (25%). Moreover, in the remaining period of investigation, NH_4^+-N concentrations were higher at the effluents than at the influents 1995 (Figure 6.5, Chapter 6). As in the case of P removal, the extremely poor performance of the field systems could be attributed to the unsatisfactory hydraulic design, which resulted in the actual inlet flow rates exceeding the expected values three-fold (on average) and thus increasing the inlet loading rates. As pointed out in Section 6.4 (Chapter 6)

the apparent improvement in the ammonium removal by approximately 30-40% in the spring of 1996 (Figure 6.8, Chapter 6) is more likely to have been caused by the precipitation during winter months, than by a real improvement in the performance.

The relatively poor efficiency of NH_4^+-N removal, in CWS systems, has been mainly attributed to the fact that the amount of O_2 present (either through release from the roots or entering the systems from the surface) is not sufficient to support nitrification. Therefore, it has been suggested that the efficiency of CWS for N removal could be improved by introducing a vertical-flow design, employing intermediate loading, or employing passive air pumps or mechanical pre-treatment units which would enhance nitrification (Brix, 1993; Haberl *et al*, 1995; Green *et al*, 1997), or by adding an external carbon source (methanol), to enhance the activity of denitrifying bacteria (Laber, 1997) (Section 1.7.5.6.). Such changes in the CWS design have improved their potential for N removal to between 80% and 93% (Laber, 1997; Sconborn *et al*, 1997).

Faulkner and Richardson (1989) stated that N removal efficiencies via CWS up to 70 % could be achieved for inlet loading rates of between 20 and 30 g N m^{-2} y^{-1}. The pilot-scale shale based systems in this study were fed with 180 g N m^{-2} y^{-1} and still maintained 99% efficiency in planted systems after 11 months of operation. This confirms that planted systems can have a very high efficiency for N removal, but it can not be determined from the present study whether the nature of the substrate played any significant role in this.

8.3. Conclusions from present work

8.3.1. Substrate life expectancy

Bavor *et al* (1995) defined the life expectancy of a CWS as the period of time over which sustainable pollutant removal can be achieved at its mean loading rate and pointed out that it is particularly critical in the case of phosphorus. They further stated

that design life expectancies have only been estimated to a limited extent and that the uncertainty in relation to P presents a critical concern when assessing the practical application of the CWS technology for waste water treatment. This is because it is well known that phosphate accumulation in wetlands is a finite process and once the systems is saturated it has to be replaced (Richardson and Davis, 1993; Hiley, 1995). Consequently, life expectancy of a CWS (designed for P removal) is dependent on the capability of the wetland substrate to adsorb P.

Because of the poor performance of the full-scale systems (Chapter 6) and the relatively short monitoring period, the results from this thesis are not sufficient to forecast accurately the lifetime of a CWS using shale as a substrate. However, data obtained from the batch experiment using phosphate solution (Table 2.4, Section 2.3) and the saturation point of the substrate (Figure 2.3, Section 2.3) can be used to provide an initial estimate.

If the observed saturation capacity were to be applied at a field scale, then one tonne of shale could be expected to absorb in excess of 0.7 kg of P. The quantity of phosphate (PO_4) excreted per person per day is 3 g (Laak, 1986). In addition 4 g PO_4 per person per day is discharged from cleaning compounds (Laak, 1986). This amounts to a total of 7 g of PO_4 (or 2.3 g of P) per person per day. Most CWS use a septic tank or similar settlement chamber as a primary treatment, to remove half of the phosphorus in the accumulated sludge, resulting in a discharge to the CWS of *ca.* 1.2 g per person per day. Assuming the land area required to treat waste water from one person is 5 m^2, and the depth of the bed is 0.6 m (EC/EWPCA, 1990), 30 m^3 or 45 tonnes of substrate would be needed to treat the effluent from 10 people. If 12 g P d^{-1} is excreted by those 10 people, the total input of P per year amounts to 4.4 kg. If 45 tonnes of the shale substrate are used, and saturation is reached at 0.7 g P kg^{-1} (Figure 2.3 b, Chapter 2), the total potential adsorption is 31.5 kg P, which in theory, suggests a lifetime of 7 years. The pilot scale CWS established in a green-house (Chapter 3, Section 3.4) showed that P adsorptive capacity is even higher, reaching the values of 0.84 g P kg^{-1} and 0.87 g P kg^{-1} in the planted and unplanted tanks

respectively, suggesting a lifetime of 9 years. As outlined in Chapter 2, P adsorptive capacity depends, in general, on the surface area of the substrate, which in this particular case, will depend on the mesh sizes used to screen the shale. In practice there has to be a compromise between surface area (inversely proportional to size) and hydraulic conductivity and so, the substrate particles should be chosen to be neither too fine, nor too coarse.

Alternatively, adopting the design guidelines from Norway, which allow a land area of 10 m^2 per person and a depth of 0.9 m (Maehlum *et al*, 1995), on the basis of these calculations the life of the system could be increased to over 20 years. Such calculations necessarily assume that flow through the substrate is well-distributed to avoid channelling, but nevertheless they indicate considerable longevity may be possible in a well-designed flow regime.

The life expectancy of a shale-based CWS could also be enhanced by including an unplanted 'forebay' containing one tonne of shale per person at the inlet to the CWS. This substrate could be excavated on an annual basis, which would result in an increase in P retention and extend the life expectancy of the main planted CWS.

The extremely high efficiency for both P and N removal (Section 8.1.1) and the estimated life expectancy of shale-based CWS could open a new direction in the design of CWS, given that results from the literature to date indicate a typical life span of CWS for P removal of only 2 - 5 years (Hammer, 1989; Cooper and Findlater, 1990; Moshiri, 1993; Kadlec and Knight, 1996). Bavor *et al* (1995) stated that long-term P removal is achievable, as indicated by a limited number of studies such as those of Kadlec and his co-workers (Kadlec *et al*, 1994; Kadlec and Knight, 1996). The only other investigations that indicate high potential of CWS for P removal as well as the life expectancy are those carried out in Norway (Maehlum *et al*, 1995; Zhu *et* al, 1997). Maehlum *et al* (1995) suggested a possible life span of 20 years, but they also pointed out that it will depend on several other parameters, such as plant root development, loading rates and retention time. Zhu *et al* (1997) showed that a range

of 12 different light expanded aggregates had P adsorption capacities of 37-3460 mg P kg^{-1}. They suggested that P adsorption capacity was a function of the chemical composition of the LECAs which varies with their parent material, which is usually clay or shale.

As pointed out in Section 2.1, one of the important criteria in making a choice of the optimal substrate for a CWS is that material should be cheap and locally available. One tonne of shale costs £5 and the price would increase by £2 for every 100 km of transport distance (Mr Pearson, Wemyss Brick Co., pers. comm). Currently, there is no production of the light expanded aggregate material in the UK - it is imported from Norway (Dr Chris Turner, pers. comm). The selling price of the material is therefore bound to be higher than that of shale, due to transport costs (shipping), and would amount to approximately £45 per tonne (Geir Norden, pers. comm.). In addition, as the production of LECAs requires energy, the overall suitability and cost effectiveness of the LECA-based CWS remains to be explored.

8.3.3. The role of plants in the CWS

The role of emergent vegetation in P and N removal via CWS was outlined in Sections 1.7.4.2 and 1.7.5.5. Apart from the indirect role of plants in physical effects (filtration of the organic and inorganic matter, insulation), as well as their contribution to visual appearance, their major role is in nutrient assimilation (nutrient storage). The presence of plants also provides the additional surface area for the attachment of microbial micro-organisms and they are capable of translocation of O_2 from their stems to the rhizosphere by diffusion, thereby influencing aerobic degradation of organic matter and nitrification (Brix, 1997).

In this thesis, the contribution of *Phragmites australis* to P and N removal was estimated by measuring O_2 release from the plant roots (Section 3.3.2.2), comparing P and N removal in planted and unplanted tanks (Chapters 3 and 6), and assessing the role of *Phragmites australis* in vertical and longitudinal nutrient concentration profiles

(Chapter 4) as well as in the flow patterns (Chapter 5). In addition, an attempt has been made to investigate phosphate precipitation on root and rhizome surfaces (Chapter 7).

The experiment measuring O_2 release from roots and rhizomes of *Phragmites* was conducted (Section 3.2.2) as a preliminary study aiming to estimate the amount of O_2 in the systems which could be attributed to the presence of plants. The results were in accordance with studies carried out by other authors which show that macrophytes do release oxygen but that the amount might be insufficient to support nitrification (Gries *et al.*, 1990; Brix, 1990, 1997; Hiley, 1995; Geller, 1997).

The major emphasis was placed on monitoring the differences in P and N removal rates between planted and unplanted tanks in a shale substrate. In the case of P removal, the unplanted beds acted as a control and showed that, although the planted tanks were superior in performance, a very high treatment efficiency was always achieved by the substrate alone, throughout the whole period of investigation (11 months). The enhanced performance of planted tanks, when compared to unplanted, was also demonstrated in a field system during the first period of investigation, from June until September 1995 (Chapter 6, Figure 6.4) despite the poor hydraulic design (Sections 6.3.2 and 6.4). However, during the second investigation carried out in the field systems during a period of one week (March 29-April 3, 1996), the performance of planted systems deteriorated by 25% (Figure 6.7). As pointed out in Section 6.4, this decrease in the reduction of P could have occurred either due to the fact that the plants had not reached their maximum growth at the time of collecting of the data, but more probably, deterioration in performance of the planted system could have been caused by the increased inlet loading of the planted system (when compared with the unplanted) as well as subsequent release of phosphate which might have occurred from the dead plant material during winter. The majority of studies which have been carried out in the USA have demonstrated that as long as the CWS is designed properly, when planted systems are compared with the unplanted, the former will almost invariably show improved performance (Kadlec and Knight, 1996). However,

although aquatic macrophytes can store significant amounts of nutrients during their growing season (Lawson, 1985; Reddy and De Busk, 1987), the majority of the nutrients which have been taken up are frequently released again during winter (when plants are dormant), and so the overall contribution of plants to P removal from CWS via uptake is generally small, even if the plants are harvested (Hiley, 1995; Cooper and Green, 1995; Brix, 1995; Brix, 1997). The P mass balance, based on the total input and output P loading rates for the period July 1995-January 1996 (Section 3.3.2.1, Table 3.3) showed that P uptake by above-ground biomass represented only 2% of the total inlet loading, again in accordance with the aforementioned studies (Section 3.4). The results from this thesis therefore suggest that plants account only for a small portion of the removed P and that the majority of P removal occurs due to physical/chemical reactions with the substrate, or incorporation into biological films.

However, the results of the spatial distribution of nutrient concentrations (Chapter 4) have revealed that although both planted and unplanted tanks followed a similar pattern of nutrient distribution, the presence of plants did have a significant effect on P concentrations at all depths (except in November 1995) and throughout the length of the tanks over the whole period of study (Section, 4.3.1, Figures 4.2 and 4.3, Table 4.1). The effect of root-zone dynamics on nutrient concentrations within CWS was also observed by Breen and Chick (1995), who indicated that significant chemical gradients can occur within the below-ground profiles of the CWS. They further suggested that the vertical differences, in particular chemical variables, can be attributed to a combination of the distribution and density of roots within the profile of systems and the hydraulics of the systems. A bromide tracer study which was carried out in order to investigate the flow patterns within shale-based CWS (Chapter 5) showed that although flow patterns were similar in both planted and unplanted tanks, with significant differences ($0.02 < p < 0.05$) between the bottom of the tanks (35 cm) and the two upper zones (20 and 10 cm) (Section 5.3., Figures 5.1. and 5.2), the difference in Br concentration between planted and unplanted tanks was significant ($p < 0.02$). This confirmed that the presence of below-ground biomass created different flow characteristics in the planted and unplanted systems. The

heterogeneous flow mechanisms between planted and unplanted CWS were also observed in the bromide tracer study carried out in the field in the spring of 1996 (Figures 6.9 and 6.10 and Section 6.4).

As outlined in Section 5.4, plants may have negative effects on the hydraulic regime of the wetlands, through channelling the flow around the root mass thus causing short-circuiting, and this has been reported by several authors (Bowmer, 1987; Marsteiner et al, 1996). In their study of the root-zone dynamics in constructed wetlands, Breen and Chick (1995) concluded that root biomass developed in the upper zone of the wetland system tends to direct flow towards the lower zone, which becomes the path of least resistance. However, the fact that a major portion of the flow travelled through the basal regions in unplanted as well as planted tanks in the present study suggests that the development of root biomass may not have been a major cause of the occurrence of preferential flows in wetland systems. As stated in Section 5.4, other factors, such as the location of the inlet zone, inlet and outlet arrangements (Steiner and Freeman, 1989; Cooper, 1993; Copper et al, 1996) or difference in chemical gradients along the wetland (Breen and Cheek, 1995) should also be taken into account.

Examination of precipitation on the surface of plant roots confirmed the potential of *Phragmites* for both P and metals retention (Chapter 7, Figures 7.1. and 7.2), although it was not possible to quantify the exact amount of deposited P. Additional laboratory analyses, combining XRD with scanning electron microscopy would be necessary to identify mineral transformations which can occur on both root and substrate surfaces.

The amount of mineral N (NH_4^+-N + NO_3^--N) which can be removed from wastewater via CWS by plant uptake is generally regarded as small compared with likely inputs. It depends on the influent loading rates, characteristics of the substrate, aeration, development of the root biomass and the presence of micro-organisms (Kadlec and Knight, 1996; Wood, 1995; Brix, 1997). However, as outlined in Chapter

3, (Section 3.4) the removal of N via above-ground biomass in this project accounted for just over 50% of the total input loading rates (Chapter 3, Table 3.4). Moreover, the work showed that NH_4^+-N was completely removed in planted tanks (Chapter 3, Figure 3.4), which suggests that the contribution of plants was substantial. Similar results have been observed in studies by other authors (Breen and Chick, 1995; Kadlec and Knight, 1996). However, as outlined in Chapter 3, (Section 3.4) the differentiation between plant uptake and other mechanisms of NH_4^+-N removal is difficult because the below-ground biomass uptake was not evaluated. Although the production of NO_3^-- N was not observed in planted tanks, and NO_3^--N concentrations were extremely low in both planted and unplanted tanks throughout the period of investigation, NH_4^+-N could have been nitrified to NO_3^-, which could then be assimilated into the plant biomass (Zhu and Sikora, 1995; Sikora *et al*, 1995).

Despite high efficacy in N removal which was achieved in planted CWS in a greenhouse, the performance of field systems in N removal was disappointing, with NH_4^+-N concentrations at the outlets of planted system often exceeding the outlet concentrations of the unplanted system during the first period of investigation (June - September 1995) (Chapter 6, Figure 6.5). The improved performance of planted systems which was observed during the second period of investigation in the field (March 29 - April 3, 1996) could have been attributed to several factors (Chapter 6, Section 6.4). The accumulation of dead plant material and litter during winter could have enriched the systems with a carbon source, which could have stimulated the processes of denitrification (Green, 1997). Also, the precipitation during the winter months could have resulted in the dilution of the water in both planted and unplanted system, which might have improved sedimentation and filtration of organic matter, thus contributing to an overall improvement in the system's performance. Lastly, the plants were at the beginning of their growing season, when they require N supply at higher rates than during summer months (Lowson, 1977; Reddy and De Busk, 1987). However, plants generally have limited nutrient assimilation capacity and during their senescence, the nutrients which were taken up during the growing season are

frequently released back to the water body (Richardson, 1985; Kadlec and Knight, 1996; Wood, 1995).

In addition to their capacity for P and N removal, the greenhouse CWS demonstrated the potential of *Phragmites* to remove Fe and Mn (Chapter 3; Table 3.3). Hadjihristova (1994) suggested that many varieties of wetland plants are tolerant of unusually high concentrations of metals because of the protective effect of iron plaque which can develop around the roots.

Spatial distributions of nutrient concentrations in the greenhouse CWS have revealed that the presence of plants did have a significant effect ($p < 0.01$) on NH_4^+-N concentrations at all depths and distances along the tanks, with planted tanks having lower concentrations throughout the period of investigation (Chapter 4, Section 4.3.2). In addition, Br tracer studies showed that there was a significant difference ($p < 0.02$) between flow patterns between planted and unplanted tanks (Chapter 5, Section 5.3). The same behaviour was observed in the field systems (Chapter 6, Section 6.3.2).

It has been claimed that plants provide adequate O_2 supply via diffusion in the aerenchyma thus contributing to the oxidative degradation of the organic material and N compounds. However, results from the various studies conducted across the world demonstrate that, in practice, the amount of O_2 that can reliably be expected to be released by plant roots and rhizomes is minimal in most horizontal systems employing subsurface flow, and the effect is limited to the immediate environment around the roots (Armstrong, 1990; Brix, 1994b; 1997). The wastewater which passes through the plant mass and surface litter biofilter is subjected to both aerobic and anaerobic environments, filtering out suspended solids and organic compounds. The plants and associated litter layer also provide a natural odour biofilter and add an aesthetic and environmental appeal to the wastewater treatment unit. The role of emergent plants in CWS and natural wetlands could be critically important, and if so their proper management will contribute to the overall efficiency and longevity of the system

(Mitchell *et al*, 1995). The emergent macrophytes are adapted to growth in highly organic, anaerobic sediments and are capable of tolerating 'shock' intermittent loads of effluents. They also modify the chemical environment of their rhizosphere, facilitating a wide range of chemically and bacteriological mediated transformations which collectively serve to improve water quality. As such, they are an indispensable component of a CWS.

8.4. Uncertainties and the need for further research

8.4.1. Longevity of full-scale systems

Although the performance of the pilot-scale CWS using shale as a substrate demonstrated a very high P and N removal efficiency from waste water (Section 8.1.2), it is still difficult to say whether the results obtained from this pilot-scale study, set up in a greenhouse, are representative of larger-scale systems. The performance of CWS mainly depends on the characteristics of the applied waste water, substrate and loading rates (Maehlum, 1995; Geller, 1997). Problems experienced with connecting the pilot-scale CWS to a supply of real sewage were described in Section 3.2.1. Although synthetic sewage has been successfully used as a substitute for real sewage in wastewater treatment studies in the UK (information supplied by WRC, Swindon), the measurements of BOD, which were carried out as part of a separate study during April and May 1996, revealed that BOD loadings were between 75 and 150 g m^{-3} (Elloriaga, 1996), these values being typical of sewage that has already passed through the first stages of treatment. This was an important observation for the estimation of the performance of the full-scale systems, given that biological growth on substrate particle surfaces (biofilm) can reduce P sorption capacity (Maehlum *et al*, 1995; Hiley, 1995).

Several researchers have stated that very often full-scale systems are not able to achieve or maintain the performance that was predicted from the studies on small-scale projects. For example, Bastian and Hammer (1993) and Mitchell *et al* (1995)

pointed out that pilot-scale systems are often isolated from sun, wind and precipitation and therefore atmospheric conditions are different from those of the full-scale systems. In addition, small-scale systems have a favourable area: volume ratio, making them difficult to reproduce at the full scale. The latter systems are also characterised by greater irregularities in substrate size, shape and placement, resulting in different hydraulic conditions (King *et al*, 1997). Also, in full-scale systems, the time required for plants to reach their full growth is extended and therefore these systems take longer to mature (Bastian and Hammer, 1993; Mitchell *et al*, 1995).

The efficiency of shale as a substrate in a full-scale field system (in this particular study) was difficult to assess, due to its poor functioning. Problems experienced with the pre-treatment unit emphasised the importance of this component in the design of a CWS (Chapter 6). The same observation has been made by Geller (1997) in his summary of the long-term practical experiences with horizontal subsurface flow systems in German-speaking countries. He also stated that the main operational work lies in maintaining the pre-treatment.

As pointed out in Section 6.5, the investigation of the use of shale as a substrate opens a new direction in the design of CWS, as most of the systems built to date in the UK use gravel as a substrate (Cooper *et al*, 1996). Shale demonstrated a high efficiency for removing P and N from wastewater (which had passed through the primary stage of treatment) and capability to cope with peak loads. However, because of the problems with the hydraulic design of the field system, the application of shale in full-scale systems remains a subject for further investigation. In the last few months, such a system has been designed for the Scottish Borders which is intended to be based on this substrate (C.A. Frost, pers. comm).

8.4.2. Processes - physical, chemical, microbial

Processes involved in P and N removal via CWS are discussed in Chapters 2 and 3 respectively. Phosphorus removal in a wetland occurs through a combination of

processes: substratum adsorption, chemical precipitation, plant and algal uptake, bacterial action and incorporation into organic matter, of which the substrate adsorption may play the greatest role (Sections 1.7.4 and 2.1). This thesis has addressed the problem of P removal via CWS (Section 8.2.1) through an investigation of the physical and chemical properties of the phosphate-removing substrates. On the basis of this investigation, a substrate was selected which was not only cheap and locally available, but also showed the greatest potential for P removal (Chapter 2). A series of experiments were conducted which demonstrated that a significant amount of P (0.65-0.70 g P kg^{-1} shale) can be removed from wastewater through the processes of physico-chemical adsorption onto the substrate (Section 2.3.2). It was not possible in the current study to quantify microbial uptake of P because it was impractical to sterilise the large quantities of shale and volumes of wastewater that were used for the experiments. It is important to conduct such an experiment in the future and this could be achieved using similar equipment to that described in Section 2.2.2.3, where the material would be sterilised, to destroy micro-organisms, prior to the passage of waste water. This would help to determine the relative amounts of P which are removed via CWS resulting from physico-chemical and microbial processes. It should, however, be noted that sterilisation by autoclaving could cause changes in the chemical composition of the material, and it might be preferable to use irradiation methods. A large proportion of the nutrients which can be taken up from the system via micro-organisms will be re-released during winter. Davis and Cottingham (1993) pointed out that once a steady-state of biomass is reached within the CWS no further removal of P will occur. In addition, Maehlum *et al.* (1995) stated that biological growth on substrate surfaces (biofilm) could reduce the P sorption capacity of the material.

Although the planted tanks were superior in performance throughout the period of investigation, the actual P uptake by plants contributed to only 2% of the total inlet P loading (Section 3.4). In addition, no experiments were conducted to investigate the uptake by algae and this remains to be quantified in future investigations.

The predominant N removal mechanism in subsurface CWS is nitrification of NH_4^+-N, with subsequent denitrification of the NO_3^--N to form nitrogenous gas products which can escape to the atmosphere (Section 1.7.5). The dissolved oxygen (DO) in subsurface flow CWS is generally low and consequently, nitrification is considered the rate limiting step for N removal (Davis and Hart, 1990; Sikora *et al*, 1995). However, it is generally believed that although low DO concentrations in CWS can inhibit nitrification, it can still occur at faster rates in the rhizosphere where DO concentration can be higher due to the plant's root oxygen release rates (Section 1.7.5.5). Ammonium removal from waste water was a secondary objective of this thesis (Section 1.8) and as such was estimated through a long-term monitoring of the difference in performance between planted and unplanted tanks in a greenhouse experiment. Because of the time limitation, no experiments were conducted to investigate NH_4^+-N adsorption onto shale particles, and this has yet to be investigated. In addition, no experiments were conducted to measure nitrification or denitrification rates. However, the fact that NO_3^--N concentrations were extremely low throughout the period of investigation (Chapters 3 and 4) indicates that denitrification occurred at a rapid rate in the systems once NH_4^+-N was nitrified. The nitrification process may have been supported at the air-water interface, where enough O_2 could have been supplied to nitrifiers via diffusion in a layer 1-2 cm in depth (Mitch and Goselink, 1993; Sikora *et al*, 1995).

As pointed out in Section 3.4 (Chapter 3), the difference in NH_4^+-N removal between planted and unplanted tanks could have been due to plant uptake, as mineral N removal via aboveground plant biomass accounted for just over 50% of the total N input loading rates. The differentiation between plant uptake and other mechanisms involved in NH_4^+-N removal is difficult because the belowground biomass uptake and rates of these processes were not evaluated. Also, due to the large number of factors that affect N removal via CWS, it is difficult to quantify the influence of each factor separately (Section 3.4). The performance of the greenhouse tanks (Chapter 3)

suggests that both mechanisms (plant uptake and nitrification/denitrification) may have been involved, resulting in greater removal rates in the planted than the unplanted tanks. It should also be taken into account that processes other than nitrification, such as microbial immobilization and adsorption should also be considered as potentially important mechanisms for removal of NH_4^+-N in subsurface flow systems. However, similarly to P uptake by microorganisms, most of the N which could be taken up by immobilization can be re-released to the water column (Section 3.4). An interesting investigation for the future could be to study the influence of carbon on N removal.

8.4.3. Comparison of performance with other systems

Data on performance of CWS in P removal are relatively sparse. Moreover, a comparison between removal efficiency and life expectancy of the systems is difficult because of the differences in operational parameters such as the loading rate, age of the system, hydraulic design (subsurface, overland or vertical flow), type of pre-treatment unit used, conditions of the vegetation, and the physical and chemical properties of the substrate.

The majority of the CWS systems established in UK practice use gravel, with typical sizes of 3-6 mm or 5-10 mm (Cooper and Green, 1995; Cooper *et al*, 1996). Given the promising performance of shale as a substrate which is demonstrated in this thesis, further research could involve a direct comparison between the nutrient removal performances of gravel and shale based CWS systems in both greenhouse and full-scale systems.

8.4.4. Problems with the hydraulic design

Pre-treatment prior to the CWS is necessary to remove coarse and heavy solids. A septic tank, properly sized, built and maintained according to the appropriate national

regulations could provide a good pre-treatment unit (Steiner *et al*, 1995; Geller, 1997).

In their review of wetland systems in Australia, Mitchell *et al* (1995) pointed out that both natural wetlands and CWS exhibited severe hydraulic short-circuiting, which resulted in inadequate treatment of waste water and low quality of the effluent. They further stated that short-circuiting problems are almost inevitable in continuous-flow systems and require intervention either in the design of the system or in its maintenance. To operate correctly, a subsurface flow CWS must initiate and maintain all or most of the flow subsurface and horizontally through the permeable media (Kadlec and Knight, 1995; Cooper *et al*, 1996). In their performance evaluation carried out on subsurface flow systems in the USA, Reed and Brown (1995) concluded that surface flow which had occurred was caused by inadequate hydraulic design and not by clogging. The further stated that flow design in subsurface flow systems should be based on Darcy's law (Section 1.7.3, Equation 3) and that an essential part of the CWS design is to accurately determine hydraulic conductivity and porosity of the media to be used as a substrate in a CWS (Chapter 2). In their reviews of CWS performance in the UK Cooper (1993) and Cooper and Green (1995) stated that weirs should not be used for flow distribution because not only were they expensive to construct but they also contribute to maldistribution of flow, which is often caused by screenable material collecting on the edges. In addition, the channel tends to act as a sedimentation tank and collects sludge and grit. Similar effects were observed in the Valleyfield full-scale systems (Chapter 6).

Because of these problems experienced with the inlet flow distribution, there has been a tendency to move to using a single manifold pipe with adjustable tees or orifices spread along its length, where the size of the pipe and tees is dictated by the flow rate (Appendix 5). However, Cooper and Green (1995) stated that these have not proved ideal, either, and that the inlet flow distribution is one area where there is still need for development. It is generally believed that, whichever system is used, it has been usual to distribute the flow onto a 0.5 m wide area of large graded stones 50 - 200 mm in

size, in an inlet area at the head of the bed (Cooper and Green, 1995; Cooper *et al*, 1996). It has been found that wire mesh gabions are useful to retain the inlet zone stones in position while the media are being placed in the bed. The inlet zone stones also serve as a secondary distributor and allow the level of water across the bed to be equalised (Cooper, 1993).

The outlet collector is one area where the original design has worked well and the system has not changed much over a decade. At the outlet end of the bed most systems have a perforated agricultural drain-pipe enclosed in a 0.5 m wide gabion filled with large graded stones (50 to 200 mm) (Cooper and Green, 1995). It is essential to provide a method for raising and lowering the water level in the bed. Cooper (1993) recommended several ways:

i) to use a 90°-elbow with 'O-ring' seals which allow the end of the pipe to be raised or lowered by swivelling at the elbow (Appendix 6);

ii) the vertical outlet pipe can consist of a series of socketed sections which can be removed to drop the water level;

iii) a piece of flexible pipe can be clamped in the required position. It is recommended that the outlet arrangement should allow the water level to be maintained at any position between 20 cm above the bed surface and the base of the bed (i.e. liner level). In addition, arrangements should be provided to allow for the outlet pipe to be flushed clean.

Apart from the inlet distribution and outlet collection systems, one should be particularly careful during the placement of the substrate in the CWS. For example, the top of the substrate surface should be flat, in order to facilitate water level control, vegetation planting and growth, and prevent the formation of stagnant pools (Steiner *et al*, 1993).

Maehlum *et al* (1995) stated that the design variables for a CWS include: characteristics of applied wastewater, hydraulic loading, characteristics of the substrate, retention time, control of flow path, type of vegetation and vegetation

management. To optimise wetland treatment performance, it has been suggested that different macrophyte-based wastewater treatment systems (for example employing vertical or horizontal flow) should be combined with each other or with conventional treatment technologies; these are called multistage systems (Brix, 1993; Wood, 1995).

The results from this thesis are in agreement with the idea of multistage systems. Such system could consist of the following units:

i) mechanical pre-treatment unit; a bar screen and a settlement tank or septic tank; in this unit settleable solids could be removed by sedimentation. In addition, BOD concentration would be decreased, which is a prerequisite for a successful N and P removal.

ii) several vertical-flow CWS laid out in parallel, planted with *Phragmites*; In these units, the substrate (shale or gravel) would be kept largely aerobic by oxygen diffusion from the atmosphere through the substrate surface and from the bottom via the drains, which would enhance nitrification and consequently N removal from the waste water. In addition, the vertical-flow units could be set up to have alternating loading (2-3 days of loading and 4-6 days of drying). In this case, air could also be drawn into the substrate during the drainage cycle. In addition, during the drying period, the suspended solids on the substrate surface would dry out and thus counteract clogging.

iii) two or more horizontal subsurface-flow CWS with continuous water saturation, laid out in parallel, planted with *Phragmites*; shale is recommended as a substrate with a high phosphorus fixing capacity. *Phragmites* would take up some of the remaining nutrients in the effluent.

A multistage system of this kind has several advantages over the single unit systems: with such a design, it is possible to regulate the loading pattern in the different units of the system in accordance with sewage production and composition. Furthermore, it is possible to take one or several units out of operation without having to disconnect the sewage from the whole system. Flexibility of design is also enhanced by providing conditions to use different kinds of macrophytes, different substrates and flow patterns. Further studies are required to improve the understanding of the removal

processes, before the most appropriate system or combination of systems can be selected and applied at a wider scale.

Bibliography

Adeloye, A.J. and Low, J.M. (1996). Surface-water abstraction controls in Scotland. *Journal of Water and Environmental Management* **10**: 123-129.

Adriano, D.C. and Doner, H.E. (1982). Bromine, chlorine and fluorine. In: Page, A.L. (ed). *Methods of soil analysis: part 2.* 2nd ed. American Society of Agronomy, Inc., Madison, Wisconsin, pp. 449-483.

Armstrong, W. (1979). Aeration in higher plants. In: Woolhouse H.W.W. (ed), *Advances in botanical research.* Academic press, London, pp 226-332.

Armstrong, W., Armstrong, J. And Beckett, P. M. (1990). Measurement and modelling of oxygen release from roots of *Phragmites australis*. In: Cooper, P.F. and Findlater, B.C. (eds), *Constructed Wetlands in Water Pollution Control.* Pergamon Press, Oxford, pp 41-51.

Bácskai, Z. (1993). *Phosphorus removal from sewage by reed bed treatment systems.* Unpublished MSc thesis, University of Manchester.

Balmér, P. and Hultman, B. (1988). Control of phosphorus discharges: present situation and trends. *Hydrobiologia*, **170**: 305 - 319.

Bastian, R.K. and Hammer, D.A. (1993). The use of constructed wetlands for wastewater treatment and recycling. In: Moshiri, G.A. (ed), *Constructed Wetlands for Water Quality Improvement*, Lewis Publishers. Baco Raton, Florida, pp 59-69.

Bavor, H. J., Roser, D.J., Fisher, P.J. and Smalls, I.C. (1989). Performance of solid-matrix wetland systems, viewed as fixed-film bioreactors. In: Hammer,

D.A. (ed.) *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural.* Lewis Publishers, Inc., Chelsea, MI, USA.

Bavor, H.J., Roser, D.J. and Adcock, P.W. (1995). Challenges for the development of advanced constructed wetland technology. *Water Science and Technology*, **32** (3): 13 - 20.

Best, N.R. (1985). Natural wetlands - southern environment. In Reddy, K.R. and Smith, W.H. (eds), *Aquatic plants for water treatment and resource recovery.* Magnolia Publishing Inc., Orlando, Florida, pp 99 - 120.

Best, E. K. (1976). An automated method for determining nitrate - N in soil extracts. *Queensland Agricultural Journal* **33**: 161 - 165.

Boon, A.G. (1985). Report on a visit by members and staff of Wrc to germany to investigate Root-Zone Method for treatment of wastewaters. Wrc Report 367/S/1. Stevenage, UK. August 1985.

Bowmer, K.H. (1987). Nutrient removal from effluents by an artificial wetland: influence of rhizosphere aeration and preferetial flow studied using bromide and dye tracers. *Water Resources*, **21** (5): 591 - 599.

Breen, P.F. and Chick, A.J. (1995). Rootzone dynamics is constructed wetlands receiving wastewater: a comparison of vertical and horizontal flow systems. *Water Science and Technology*, **32** (3): 281-291.

Bremner, J.M. (1965). Total Nitrogen. In: Black, C.A., Evans, D.D., White, J.L., Ensminger, L.E. and Clark, F.E. (eds) *Methods of soil analysis, Part 2. Chemical and microbiological properties.* American Society of Agronomy, Madison, Wisconsin, USA, pp 1149-1178.

Brix, H. (1987). Treatment of wastewater in the rhizospehere of wetland plants - The root-zone method. *Water Science and Technology*, **19**: 107-118.

Brix, H. (1990). Gas exchange through soil-atmosphere interphase and through dead culms of *Phragmites australis* in a constructed reed bed receiving domestic waste. *Water Research*, **24**: 259-266.

Brix, H. (1991). The use of macrophytes in waste water treatment: biological features. In Madoni, P. (ed.) *Biological Approach to Sewage Treatment Process: Current Status and Perspectives*, Perugia, Italy, pp. 321-328.

Brix, H. (1993). Constructed wetlands for municipal wastewater treatment in Europe. In: Mitsch, W.J. and Gosselink, J.G (eds.), *Wetlands*. 2nd edition, Van Nostrand Reinhold, New York, pp 439 - 450.

Brix, H. (1994a). Use of constructed wetlands in water pollution control: historical development, present status and future perspectives. Paper presented at *IAWQ Biennial Conference*, Budapest, Hungary, July 1994.

Brix, H. (1994b). Functions of macrophytes in constructed wetlands. *Water Science and Technology*, **29** (4): 71-78.

Brix, H. (1997). Do macrophytes play a role in constructed treatment wetlands? *Water Science and Technology*, **35** (5): 11-17.

Brix, H. and Schierup H. (1989). The use of aquatic macrophytes in water-pollution control. *Ambio*, **18**, 100-107.

Brown, G and Brindley, G.W. (1980). X-ray diffraction procedures for clay mineral identification. In: Brindley, G.W. and Brown, G (eds). *Crystal structures of clay minerals and their X-ray identification*. Mineralogical Society Monograph No

5. Mineralogical Society, London, pp 305-361.

Buchberger, S. G. and Shaw, G. B. (1995). An approach toward rational design of constructed wetlands for wastewater treatment. *Ecological Engineering*, **4** (4): 249 - 275.

Bucksteeg, K. (1990). Suitablility of different biological sewage treatment systems. *Water Science and Technology*, **22**: 187-194.

Chan, E., Bursztynsky, T.A., Hantzsche, N.N and Litwin, Y.J. (1981). The use of wetlands for water pollution control. U.S. EPA Grant No. R-806357.

Chang, S.C. and Jackson, M.L. (1957). Fractionation of soil phosphorus. *Soil Science*, **84** (2): 133-144.

Conley, L.M., Dick, R.I. and Lion, L.W. (1991). An assessment of the root zone method of wastewater treatment. *Jornal WPCF*, **63** (3): 239-247.

Cooke, J.G. (1992). Phosphorus removal processes in a wetland after a decade of receiving a sewage effluent. *Journal of Environmental Quality* **21**: 733-739.

Cooke, G.D., Welch, E.B., Martin, A.B., Fulmer, D.G., Hyde, J.B. and Schrieve, G.D (1993). Effectiveness of Al, Ca, and Fe salts for control of internal phosphorus loading in shallow and deep lakes. In: Boers, P.C.M., Cappenberg, T.E. and van Raaphorst, W. (Eds). *Proceedings of the Third International Workshop on Phosphorus in Sediments*. Kluwer Academic Publishers, Belgium, pp 323-337.

Cooper, P.F. (1993). The use of reed bed systems to treat domestic sewage: the European design and operation guidelines for reed bed treatment systems. In: Moshiri, G.A. (ed), *Constructed Wetlands for Water Quality Improvement*, Lewis Publishers. Baco Raton, Florida, pp 203-219.

Cooper, P.F. and Findlater, B.C. (eds) (1990). *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford.

Cooper, P. and Green, B. (1995). Reed bed treatment systems for sewage treatment in the United Kingdom - the first ten years of experience. *Water Science and Technology*, **32** (3): 317 - 327.

Cooper, P. F., Day, M. and Thomas, V. (1994). Process options for phosphorus and nitrogen removal from wastewater. *Journal of Institute of Water Environmental Management*, **8**: 84 - 92.

Cooper, P. F., Hobson, J. A. & Jones, B. A. (1989). Sewage treatment by Reed Bed Systems. *Journal of Institute of Water Environmental Management*, **3**, 60-74.

Cooper, P. F., Job, G.D., Green, M.B. and Shutes, R.B.E. (1996). Reed beds and constructed wetlands for wastewater treatment. Proceedings of the *Water Research Council/Severn Trent Water Workshop on "Reed Beds and Constructed Wetlands"*, Kenilworth, Warwickshire, June 1996. WRc Ltd., Swindon.

Crooke, W.M. and Simpson, W.E. (1971). Determination of ammonium in Kjeldahl digests of crops by an automated procedure. *J.Sci.Fd. Agric.* **22**: 9 - 10.

Culp, R.L., Wesner, G.M. and Culp, G.L. (1978). *Handbook of Advanced Wastewater Treatment*. 2nd ed., Van Nostrand Reinhold Company, New York.

Daigger, G.T. and Polson, S.R. (1991). Design and operation of biological nitrogen removal facilities. In: Sedlak, R (ed), *Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice*. 2nd ed., Lewis Publishers, New York, pp 43 - 88.

Davies, T.H. and Hart, B.T. (1990). Use of aeration to promote nitrification in reed beds treating wastewater. In: Cooper, P.F. and Findlater, B.C. (eds), *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford, pp 77-85.

Davies, T.H. and Cottingham, P.D. (1993). Phosphorus removal from wastewater in a constructed wetland. In: Moshiri, G.A (ed.), *Constructed Wetlands for Water Quality Improvement*, Lewis Publishers, Boca Raton, Florida, pp 315 - 320.

DeBusk, T.A. and Ryhter, J.H. (1987). Biomass production and yields of aquatic plants. In: Reddy, K.R. and Smith, W.H. (eds). *Aquatic Plants for Water Treatment and Resource Recovery*. Magnolia Publishing Inc. Orlando, Florida, USA, pp 337 - 359.

Department of Environment (1980). Analysis of Raw, Potable and Wastewaters. HMSO, London.

Department of Environment (1981). Assessment of Biodegradability. Methods for the examination of waters and associated materials. HMSO, London.

Department of Environment (1986). Methods for the Examination of Waters and Associated Materials. HMSO, London.

Drizo, A., Frost, A., Smith, K. and Grace, J. (1997). Phosphate and ammonium removal by constructed wetlands with horizontal subsurface flow, using shale as a substrate. *Water Science and Technology*, **35** (5): 95-102.

EC/EWPCA (1990). European design and operations guidelines for reed bed treatment systems. Presented to the *Conference "Constructed Wetlands in Water Pollution Control"*, Cambridge, September 1990. Also available as WRc Report UI 17, WRc Swindon, December 1990.

Elorriaga, H. (1996). Pilot-scale subsurface constructed wetland performance evaluation on biological oxygen demand (BOD) and suspended solids (SS) removal from synthetic sewage. B.Sc. (Hons.) in Ecological Sciences, The University of Edinburgh.

Etnier, C. and Guterstam, B. (eds) (1991). *Ecological Engineering for Wastewater Treatment. Proceedings of International Conference at Stensund Folk College, Sweden,* March 1991. Boks Akogen, Gothenburg, Sweden.

Faulkner, S.P. and Richardson, C.J. (1989). Physical and chemical characteristics of freshwater wetland soils. In: Hammer, D.A. (ed.) *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural.* Lewis Publishers, Inc., Chelsea, MI, USA.

Fillos, J.W. and Swanson, W.R. (1975). The release rate of nutrients from river and lake sediments. *Journal of Water Pollution Control Federation,* **47:** 1032 - 1042.

Findlater, B.C., Hobson, J.A. and Cooper, P.F (1990). Reed bed treatment systems: performance evaluation. In: Cooper, P.F. and Findlater, B.C. (eds), *Constructed Wetlands in Water Pollution Control,* Pergamon Press, Oxford.

Fisher, P.J. (1990). Hydraulic characteristics of constructed wetlands at Richmond, NSW, Australia. In: Cooper, P.F. and Findlater, B.C. (eds) (1990). *Constructed Wetlands in Water Pollution Control,* Pergamon Press, Oxford, pp 21-31.

Flaig, E.G. and Reddy, K.R. (1995). Fate of phosphorus in the Lake Okeechobee watershed, Florida, USA: overview and recommendations. *Ecological Engineering,* 5 (2/3): 127 - 142.

Flury, M. And Papritz, A. (1993). Bromide in the natural environment: occurrence and toxicity. *Journal of Environmental Quality*, **22**: 747-758.

Forum (1995). Engineered reed-bed systems for wastewater treatment. *Trends in Biotechnology*, **13**: 248- 252.

Gambrell, R.P. and Patrick, W.H., Jr (1978). Chemical and microbiological properties of anaerobic soils and sediments. In: Hook, D.D. and Crawford, R.M.M (eds), *Plant Life in Anaerobic Environments*. Lewis publishers. Ann Arbor, MI, pp 375 - 423.

Gambrell, R.P., Delaune R.D. and Patrick, W.H.Jr (1991). Redox processes in soils following oxygen depletion. In: Jackson, M.B., Davies, D.D. and Lambers, H. (Eds), *Plant life under oxygen deprivation*. SRB Academic Publishing, The Hague, The Netherlands, pp 101-121.

Geller, G. (1997). Horizontal subsurface flow systems in the German speaking countries: summary of long-term scientific and practical experiences; recommendations. *Water Science and Technology* **35** (5): 157-167.

Gersberg, R.M., Elkins, B.V., Lyon, S.R. and Goldman, C.R. (1986). Role of aquatic plants in wastewater treatment by artificial wetlands. *Water Resources*, **20:** 363 - 368.

Green, M.B. and Upton, J. (1995). Constructed reed beds: appropriate technology for small communities. *Water Science and Technology*, **32** (3): 339-349.

Green, M.B., Friedler, E., Ruskol, Y. and Safrai, I. (1997). Investigation of alternative method for nitrification in constructed wetlands. *Water Science and Technology*, **35** (5): 63-70.

Gumbricht, T. (1993). Nutrient removal capcity in submersed macrophyte pond systems in a temperate climate. *Ecological Engineering*, **2**: 49 - 61.

Guntenspregen, G.R. and Stearns, F. (1985). Ecological perspectives on wetland systems. In Godfrey, P.J., Kaynor, E.R., Pelzarski, S. and Benforado, J. (eds), *Ecological Considerations in Wetland Treatment of Municipal Wastewaters.* Van Nostrand Reinhold, New York, pp 69 - 95.

Haberl, R., Perfler, R. And Mayer, H. (1995). Constructed wetlands in Europe. *Water Science and Technology*, **32** (3): 305-317.

Hadjichristova, M. (1994). Unpublished thesis, University of Manchester, UK.

Hammer, M.J. (1986). *Water and Wastewater Technology.* 2nd ed. John Wiley and Sons, New York.

Hammer, D.A. (ed.) (1989) *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural.* Lewis Publishers, Inc., Chelsea, MI, USA

Hammer, D.A (1992). *Creating Freshwater Wetlands.* Lewis Publishers, Inc., Chelsea, MI, USA.

Hammer, D.A. and Knight, R.L. (1994). Designing constructed wetlands for nitrogen removal. *Water Science and Technology*, **29** (4): 15 - 27.

Hantzsche, N.N (1985). Wetland systems for wastewater treatment: engineering applications. In: Godfrey, P.J., Kaynor, E.R., Pelzarski, S. and Benforado, J. (eds), *Ecological Considerations in Wetland Treatment of Municipal Wastewaters.* Van Nostrand Reinhold, New York, pp 12-23.

Harper, D. (1995). *Eutrophication of Wastewaters*. 2nd ed. Chapman and Hall, London.

Harrison, P. (1988). UK soils: their phosphorus removal capacity and potential for phosphorus removal from sewage effluents in emergent hydrophyte treatment systems. ITE Merlewood Research Station Report, 1988.

Hedin, R.S. and Nairn, R.W. (1989). Sizing and preformance of constructed wetlands: case studies. In: Skousen, J., Sencidiver, J. and Samuel, D. (eds). *Proceedings of the 1990 Mining and Reclamation Conference and Exibition, Vol II.* West Virginia University, Morgantown, Wv, pp 385 - 392.

Henze, M (1996). Biological phosphorus removal from wastewater: processes and technology. *Water Quality International*, July/August 1996, pp 32 - 36.

Heslop, R.B. and Jones, K. (1976). *Inorganic chemistry*. Elsevier Scientific Publishing Company, Amsterdam, The Netherlands.

Hiley, P. D. (1991). *The non-removal of phosphorus from sewage by constructed wetlands*. Yorkshire Water plc.

Hiley, P.D. (1995). The reality of sewage treatment using wetlands. *Water Science and Technology*, **32** (3): 329 - 338.

Hill, D.E. and Sawhney, B.L. (1981). Removal of phosphorus from wastewater by soil under aerobic and anaerobic conditions. *Journal of Environmental Quality*, **10**: 401 - 405.

Hills, J.S. (1995). *Cutting water and effluent costs*.2nd ed. Institution of chemical engineers, Rugby, Warwickshire, UK.

Horan, N.J. (1990). *Biological Wastewater Treatment Systems: Theory and Operation*. John Wiley and Sons, New York.

Horan, N.J. (1992). Nutrient removal from wastewaters. *Water and Wastewater Technology*, **2**: 16 - 17.

House of Lords (1991). Select Comittee on the European Communities. *Municipal waste water treatment*. Volume 1-Report. HMSO, London.

House of Lords (1994). *Environment Agencies Bill*. HMSO, London.

Howard-Williams, C. (1985). Cycling and retention of nitrogen and phosphorus in wetlands: a theoretical and applied perspective. *Freshwater Biology*, **15**: 391 - 431.

Hsu, P.H. (1964). Adsorption of phosphate by aluminium and iron in soils. *Soil Science Society of America Proceedings*, **28**: 474 - 478.

Hurry, R.J. and Bellinger, E.G. (1990). Potential yield and nutrient removal by harvesting *Phalaris arundinacea* in a wetland treatment system. In: Cooper, P.F. and Findlater, B.C. (eds), *Constructed Wetlands in Water Pollution Control*. Pergamon Press, Oxford.

Institute of Sewage Purification (ISP) (1960). *An Introduction to Sewage Treatment*. ISP, London.

Institution of Water and Environmental Management (IWEM) (1994). *Tertiary Treatment*. 2nd ed., IWEM, London.

Jenssen, P.D., Mæhlum, T. and Krogstad, T. (1993). Potential use of constructed wetlands for wastewater treatment in northern environments. *Water Science and Technology*, **28** (10): 149 - 157.

Johansson, L (1997). Use of LECA (Light Expanded Clay Aggregates) for the removal of phosphorus from wastewater. *Water Science and Technology*, **35** (5): 87-93.

Jones, A.A. (1990). X-ray fluorescence analysis. In: Smith, K.A. (ed). *Soil Analysis-Modern Instrumental Techniques*. Marcel Dekker, New York, pp 287-324.

Kadlec, J.A. (1987). Nutrient dynamics in wetlands. In: Reddy, K.R. and Smith, W.H. (eds), *Aquatic Plants for Water Treatment and Resource Recovery*. Magnolia Publishing Inc. Orlando, Florida, 393 - 420.

Kadlec, R.H. (1995). Overview: surface flow constructed wetlands. *Water Science and Technology*, **32** (3): 1 - 12.

Kadlec, R.H. and Knight, R.L. (1995). *Treatment wetlands*. Lewis Publishers, Chelsea, MI.

Kadlec, R.H., Bastiaens, W. and Urban, D.T. (1993). Hydrological design of free water surface wetlands. In: Moshiri, G.A.(Ed) *Constructed Wetlands for Water Quality Improvement*, Lewis Publishers Inc., Boca Raton, Florida, pp 77-87.

Kickuth, R. (1977). Degradation and incorporation of nutrients from rural wastewaters by plant rhizosphere under limnic conditions. In *Utilization of Manure by Land Spreading*, Comm. of the European Communities, EUR 5672e, London, pp. 335-343.

Kickuth, R. (1982). A low-cost process for purification of municipal and industrial waste water. *Der Tropenlandwirt*, **83**: 141-154.

King, A.C., Mitchell, C.A. and Howes, T. (1997). Hydraulic tracer studies in a pilot scale subsurface flow constructed wetland. *Water Science and Technology*, **35** (5): 189-197.

Kittrick, J.A. and Jackson, M.L. (1956). Electron microscope observation of the reactions of phosphates with minerals leading to a unified theory of phosphorus fixation in soils. *Soil Science*, 7: 81 - 89.

Knight, R.L. (1994). Treatment wetlands database. *Water Environment and Technology*, **6** (2): 31 - 33.

Knight, R.L. (1997). Wildlife habitat and public use benefits of treatment wetlands. *Water Science and Technology*, **35** (5): 35 - 45.

Knight, R.L., Ruble, R.W., Kadlec, R.H. and Reed, S. (1993). Wetlands for wastewater treatment: performance database. In: Moshiri, G.A (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers. Boca Raton, Florida.

Kuo, J., Fox, E. and McDonald, S. (1992). *SigmaStat User's Manual*. Jandel Scientific GmbH, Erkrath, Germany.

Laak, R. (1986). *Wastewater Engineering for Unsewered Areas*. 2nd ed. Technomic Publishing Co., Inc., Hague, The Netherlands.

Laber, J., Perfler, R. And Haberl, R. (1997). Two strategies for advanced nitrogen elimination in vertical flow constructed wetlands. *Water Science and Technology* **35**(5): 71-79.

Lawson, G.J. (1985). Cultivating reeds (*Phragmites australis*) for root zone treatment of sewage. ITE Project 965. Water Research Centre, Cumbria, UK.

Lindsay, W.L. (1979). *Chemical equilibria in soils*. John Wiley & Sons, Inc, USA.

Low, P.F. and Black, C.A. (1950). Reactions of phosphate with kaolinite. *Soil Science*, **70**: 272 - 290.

Lowe, N.R. (1990). The need for hydrophyte-based systems in the treatment of waste water from small communities. In: Cooper, P.F. and Findlater, B.C. (eds.), *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford.

Maehlum, T., Jenssen, P. And Warner, W.S. (1995). Cold-climate constructed wetlands. *Water Science and Technology*, **32** (3): 95-103.

Mann, R.A. (1990). Phosphorus removal by constructed wetlands: substratum adsorption. In: Cooper, P.F. and Findlater, B.C. (Eds) *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford.

Mann, R.A. and Bavor, H.J. (1993). Phosphorus removal in constructed wetlands using gravel and industrial waste substrata. *Water Science and Technology*, **27**: 107 - 113.

Marsteiner, E.L., Collins, A.G., Theis, T.L. and Young, T.C. (1996). The influence of macrophytes on subsurface flow wetland (SSFW) hydraulics. Preprints of the 5th International Conference on Wetland Systems for Water Pollution Control. Universität für Bodenkultur Wien, Vienna, Austria, pp 1-7.

Mason, C. F. (1991). *Biology of Freshwater Pollution*, 2nd ed., Longman Scientific & Technical, New York.

McEldowney, S., Hardman, D. J. and Waite, S. (1993). *Pollution: Ecology and Biotreatment*. Longman Scientific & Technical. Essex, UK.

Mitchell, D.S., Chick, A.J. and Raisin, G.W. (1995). The use of wetlands for water pollution control in Australia: an ecological perspective. *Water Science and Technology*, **32** (3): 365-375.

Mitsch, W.J. and Gosselink, J.G. (1993). *Wetlands*. 2nd ed. Van Nostrand Reinhold, New York.

Moshiri, G.A (ed) (1993). Constructed Wetlands for Water Quality Improvement. Lewis Publishers, Boca Raton, Florida, USA.

Netter, R. (1994). Flow characteristics of planted soil filters. *Water Science and Technology*, **29** (4): 37-45.

Netter, R. and Bischofsberger, W. (1990). Hydraulic investigations on planted soil filters. In: Cooper, P.F. and Findlater, B.C. (eds) (1990). *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford, pp 11-21.

Nichols, D.S. (1983). Capacity of natural wetlands to remove wetlands from wastewater. *Journal of Water Pollution Control Federation*, **55**: 495 - 505.

Olsen, S.R. and Watanabe, F.S. (1957). A method to determine phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. *Soil Science Society of America Proceedings*, **21**: 144 - 149.

Parfitt, R.L. (1978). Anion adsorption by soils and soil materials. *Advances in Agronomy*, **30**: 1 - 49.

Parfitt, R., Atkinson, R.J. and Smart,R.C. (1975). The mechanism of phosphate fixation by iron oxides. *Soil Science Society of America Proceedings*, **39**: 837 - 841.

Patrick, W.H and Khalid Jr, R.A. (1974). Phosphate release and sorption by soils and sediments: Effect of aerobic and anaerobic conditions. *Science*, **186**: 53 - 55.

Patrick, W.H and Reddy, K.R. (1976). Nitrification-denitrification reactions in flooded soils and water bottoms: dependence on oxygen supply and ammonium diffusion. *Journal of Environmental Quality*, **5**: 469-472.

Payne, W.J. (1981). Denitrification. John Wiley & sons, Inc., USA.

Petterson, K. And Istvanovics, V. (1988). Sediment phosphorus in Lake Balaton-forms and mobility. In: Psenner, R. And Gunatilaka, A. (eds) *Proceedings of the first international workshop on sediment phosphorus. Advances in Limnology*, **30**: 25-41.

Peverly, J.H., Surface, J.M. and Wang, T. (1995). Growth and trace metal absorption by *Phragmites australis* in wetlands constructed for landfill leachate treatment. *Ecological Engineering* , **5** (1): 21 - 35.

Platzer, C. and Netter, R. (1994). Factors affecting nitrogen removal in horizontal flow reed beds. *Water Science and Technology*, **29** (4): 319-325.

Ponnamperuma, F.N. (1972). The chemistry of submerged soils. *Advances in Agronomy*, **24** : 29-96.

Potter, P., Maynard, J.B. and Pryor, W.A. (1980). *Sedimentology of shale: study guide and reference source*. Springer-Verlag Inc., New York, NY.

Ramalho, R.S. (1977). *Introduction to Wastewater Treatment Processes.* Academic Press, Inc., New York.

Rawlinson, K. (1996). *A review of the use of constructed wetlands in the treatment of wastewater: with reference to the UK experience.* Unpublished MScThesis. Heriot-Watt University, Edinburgh.

Reddy, K.R. and Graez, D.A. (1981). Use of shallow reservoir and flooded organic soil systems for waste water treatment: nitrogen and phosphorus transformations. *Journal of Environmental Quality* **10** (1): 113-119.

Reddy, K.R. and Patrick, W.H.Jr (1984). Nitrogen transformations and loss in flooded soils and sediments. *Critical Reviews in Environmental Control*, **13** (4): 273-309.

Reddy, K.R. and DeBusk, W.F. (1987). Plant nutrient storage capabilities. In: Reddy, K.R. and Smith, W.H. (eds). *Aquatic Plants for Water Treatment and Resource Recovery.* Magnolia Publishing Inc. Orlando, Florida, USA, pp 337 - 359.

Reddy, K.R. and D'Angelo, E.M. (1997). Biogeochemical indicators to evaluate pollutant removal efficiency in constructed wetlands. *Water Science and Technology* **35** (5): 1-10.

Reed, S. C. (1991). Constructed wetlands for wastewater treatment. *Biocycle*, **32** (11): 44 - 49.

Reed, S.C. (1992). Constructed wetland design: the first generation. *Water Environmental Resources*, **64** (6): 776 - 781.

Reed, S.C. and Bastian, R.K. (1985). Wetlands for wastewater Treatment: an engineering perspective. In: Godfrey, P.J., Kaynor, E.R., Pelzarski, S. and Benforado, J. (eds), *Ecological Considerations in Wetland Treatment of Municipal Wastewaters.* Von Nostrand, Reinhold, New York, pp 444 - 458.

Reed, S.C. and Brown, D. (1995). Subsurface flow wetlands - a performance evaluation. *Water Environment Resources,* **67** (2): 244 -248.

Reed, S.C., Middlebrooks, E.J. and Crites, R.W. (1988). *Natural systems for waste management and treatment.* McGraw-Hill Inc., New York, NY.

Reed, S.C., Crites, R.W. and Middlebrooks, E.J. (1995). *Natural Systems for Waste Management and Treatment*, 2nd ed., McGraw-Hill, New York.

Richardson, C.J. (1985). Mechanisms controling phosphorus retention capacity in freshwater wetlands. *Science,* **228**: 1424 - 1427.

Richardson, C.J. and Craft, C.B. (1993). Effective phosphorus retention in wetlands: fact or fiction? In: Moshiri, G.A, (ed.), *Constructed Wetlands for Water Quality Improvement.* Lewis Publishers. Boca Raton, Florida, USA, pp 271 - 282.

Richardson, C.J. and Davis, J.A. (1987). Natural and artificial wetland ecosystems: ecological opportunities and limitations. In Reddy, K.R. and Smith, W.H., (eds.), *Aquatic Plants for Water Treatment and Resource Recovery.* Magnolia Publishing Inc. Orlando, Florida, USA, pp 819 - 845.

Richardson, C.J. and Marshall, P.E. (1986). Processes controlling movement, storage and export of phosphorus in a fen peatland. *Ecological Monographs* **56**: 279 - 296.

Richardson, C.J. and Nichols, D.S (1985). Ecological analysis of wastewater management criteria in wetland ecosystems. In: Godfrey, P.J., Kaynor, E.R., Pelzarski, S. and Benforado, J. (eds.), *Ecological Considerations in Wetland Treatment of Municipal Wastewaters.* Von Nostrand, Reinhold, New York, pp 351 - 391.

Ridgway, J.M. (1982). *Common clay and shale.* Series: Mineral dossier **22**, HMSO, London.

Rogers, K.H., Breen, P.F. and Chick, A.J. (1990). Hydraulics, root distribution and phosphorus removal in experimental wetland systems. In: Cooper, P.F. and Findlater, B.C. (eds) (1990). *Constructed Wetlands in Water Pollution Control,* Pergamon Press, Oxford, pp 587-591.

Rowe, D.R and Abdel-Magid, I.M. (1995). *Wastewater reclamation and reuse.* Lewis Publishers, Boca Raton, Florida, USA.

Rowell, D.V. (1994). *Soil Science: Methods and Applications.* Longman Scientific & Tecnnical, London.

Russell, S. (1994). *Ammonia.* WRc plc. Medmenham, Buckingham, UK.

Sanford, W.E., Steenhuis, T.S., Parlange, J.Y., Surface, J.M. and Peverly, J.H. (1995). Hydraulic conductivity of gravel and sand as substrates in rock-reed filters. *Ecological Engineering*, **4** (4): 321-337.

SAS Institute Inc. (1985). *SAS STAT guide for personal computers, Version* 6. SAS Institute Inc., Cary, NC, 378 pp.

Sawnhey, B.L. (1977). Predicting phosphate movement through soil columns. *Journal of Environmental Quality*, **6** : 86-89.

Schelske, C.L. (1980). Dynamics of nutrient enrichment in large lakes: The lake Michigan case. *Proceedings of Symposium on the Restoration of Lakes and Inland Waters*, U.S. EPA.

Schierup, H., Brix, H. and Lorenzen, B. (1990). Wastewater treatment in constructed reed beds in Denmark - state of the art. In: Cooper, P.F. and Findlater, B.C. (Eds) *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford, pp. 495 - 504.

Scholes, J.D., Kerr, R.I. and Nuttall, P.M. (1986). Treatment of wastewater by aquaculture systems. *Australian Water Research Council Project*, No 80/139.

Sedlak, R (1991). (ed). *Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice.* 2nd ed., Lewis Publishers, New York.

Schönborn, A., Züst, B. And Underwood, E. (1997). Long term performance of the samd-plant-filter Schattweid (Switzerland). *Water Science and Technology*, **35** (5): 307-315.

Seidel, K. (1966). Reinigung von Gewassern durch hohere Pflanzen. *Naturwiss*, **53**, 289-297.

Seidel, K. (1976). Macrophytes and water purification. In: Tourbier, J. and Pierson, R.W. Jr (eds.), *Biological Control of Water Pollution.* University of Pennsylvania Press, Philadelphia.

Seitzinger, S.P. (1990). Denitrification in aquatic sediments. In: Revsbech, N.P. and Sorensen, J (eds). *Denitrification in soil and sediment.* Plenum Press, New York, pp 301-322.

SEPA (1995). *Water Quality Objectives for the years 2000 and 2015.* Forth River Purification Board, Edinburgh.

SEPA (1996). *The State of the Environment Report 1996*. The Scottish Environment Protection Agency, Stirling, UK.

Sharpley, A.N. (1995). Soil phosphorus dynamics: agronomic and environmental impacts. *Ecological Engineering* **5**(2+3): 261-281.

Shukla, S.S, Syers, J.K, Williams, J.D.H, Armstrong, D.E. and Harris, R.F (1971). Sorption of inorganic phosphate by lake sediments. *Soil Science Society of America Proceedings*, **35**: 244 - 249.

Sikora, F.J., Zhu, T., Behrends, L.L., Steinberg, S.L. and Coonrod, H.S. (1995). Ammonium removal in constructed wetlands with recirculating subsurface flow:removal rates and mechanisms. *Water Science and Technology* **32** (3):193-203.

Sokal, R.R. and Rohlf, F.J. (1981). *Biometry*. 2nd edition. W.H. Freeman and Co., San Francisco, USA.

Somlyo'dy, L. (1994). Quo vadis water quality management in central and eastern Europe. In: *Biological Wastewater Treatment and Wetland Workshop - Handbook*. Central European University, Budapest, Hungary, 1-12.

Sorell, B.K. and Armstrong, W. (1994). On the difficulties of measuring oxygen release by root systems of wetland plants. *Journal of Ecology*, **82**: 177-183.

Stanford, G., Freere, M.H. and Schvawaninger, D.H. (1973). Temperature coefficient of soil nitrogen mineralization. *Soil Science*, **115**: 321-323.

Stark, R.L. and Williams, F.M. (1995). Assessing the performance indices and design parameters of treatment wetlands for H^+, Fe and Mn retention. *Ecological Engineering* **5** (4): 433-444.

Steiner, G.R. and Freeman, R.J. Jr (1989). Configuration and substrate design considersations for constructed wetlands wastewater treatment. In: Hammer, D.A., (ed.), *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural*. Lewis Publishers, Inc., Chelsea, MI, USA.

Steiner, G.R., Watson, J.T. and Choate, K.D. (1993). General design, construction and operation guidelines for small constructed wetlands wastewater treatment systems. In: Moshiri, G.A (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers. Boca Raton, Florida, pp 499-508.

Stensel, H.D. (1991). Principles of Biological Phosphorus Removal. In: Sedlak, R.I. (ed), *Phosphorus and Nitrogen Removal from Municipal Wastewater*. 2nd ed. Lewis Publishers, New York, NY.

Stuanes, A.O. (1984). Phosphorus sorption of Soils to be used in wastewater renovation. *Journal of Environmental Quality* **13**: 220 - 224.

Suzuki, T., Nissanka, W.G.A. and Kurihara, Y. (1989). Amplification of total dry matter, nitrogen and phosphorus removal from stands of *Phragmites australis* by harvesting and reharvesting regenerated shoots. In: Hammer, D.A., (ed.), *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural*, Lewis Publishers, Inc., Chelsea, MI, USA.

Syers, J.K., Evans, T.D., Williams, D.H. and Murdock, J.T. (1971). Phosphate sorption parameters of representative soils from Rio Grande do Sul, Brazil. *Soil Science*, **112**: 267 - 275.

Syers, J..K., Harris R.F. and Armstrong D.E. (1973). Phosphate chemistry in lake sediments. *Journal of Environmental Quality* **2**: 1-14.

Talibudeen, O. (1981). Precipitation. In: Greenland, D.J. and Hayes, M.H.B. (eds). *The chemistry of soil processes*. Pitman Press, Bath, Avon, pp 81-115.

Tanner, C.C. and Sukias, J.P. (1995). Accumulation of organic solids in gravel-bed constructed wetlands. *Water Science and Technology*, **32** (3): 229-241.

Tchobanoglous, G (1987). Aquatic plant systems for water treatment: engineering considerations. In Reddy, K.R. and Smith, W.H., (eds.), *Aquatic Plants for Water Treatment and Resource Recovery*. Magnolia Publishing Inc. Orlando, Florida, USA, pp 819 - 845.

Tchobanoglous, G (1993). Constrcuted wetlands and aquatic plant systmes: research, design, operational and monitoring issues. In: Moshiri, G.A (ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers. Boca Raton, Florida, USA.

Tchobanoglous, G (1996). Constructed wetlands: reserach, design, operational and monitoring issues. Internal Report from the *Alternative wastewater treatment systems workshop*, Agricultural University Ås, Norway, 22-29 June, 1996.

Tchobanoglous, G and Burton, F.L (1991). *Wastewater Engineering*, 3rd ed.,. McGraw-Hill, Inc, New York.

Tetreault, M.J., Benedict, A.H., Kaempfer, C. and Barth, E.F. (1986). Biological phosphorus removal: a technology evaluation. *Journal of the Water Pollution Control Federation*, **58**: 823 - 7.

Vymazal, J. (1995). Constructed wetlands for wastewater treatment in the Czech Republic-state of the art. *Water Science and Technology*, **32** (3): 357-365.

Watson, J.T and Hobson, J.A (1989). Hydraulic design considerations and control structures for constructed wetlands for wastewater treatment. In Hammer, D.A., (ed.), *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural*. Lewis Publishers, Inc., Chelsea, MI, USA, pp 379 - 393.

Watson, J.T., Reed, S.C., Kadlec, R.H., Knight, R.L. and Whitehouse, A.E (1989). Performance expectations and loading rates for constructed wetlands. In: Hammer, D.A. (ed.), *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural*. Lewis Publishers, Inc., Chelsea, MI, USA, pp 319-353.

Wetzel, R.G (1975). *Limnology*. Sounders, Philadelphia.

White, J.B. (1978). *Wastewater Engineering*. Edward Arnold, London.

Whitehead, P.G., Williams, R.J. and Hornberger, G.M. (1986). On the identification of pollutant or tracer sources using dispersion theory. *Journal of Hydrology*, **84**: 273-286.

Willadsen, C.T., Riger-Kusk,O. and Qvist, B. (1990). Removal of nutritive salts from two Danish root zone systems. In: Cooper, P.F. and Findlater, B.C. (Eds) *Constructed Wetlands in Water Pollution Control*, Pergamon Press, Oxford, pp.115-127.

Williams, J.D.H, Syers J.K, Shulka S.S, Harris, R.F and Armstrong, D.E. (1971). levels of inorganci and total phosphorus in lake sediments as related to other sediment parameters. *Environmental Science and Technology*, **5**: 1113-1120.

Wilson, H., Payne, S., O'Sullivan, P. and Gibson, M. (1996). Policy and legislation relevant to the conservation of freshwater SSSIs subject to

eutrophication. *Journal of Water and Environmental Management,* **10**: 348-354.

Williams, J.D.H, Syers J.K. Shulka S.S and Harris, R.F. (1971). *Environmental Science and Technology* **5**: 1113.

Wilson, H., Payne, S., O'Sullivan, P. and Gibson, M. (1996). Policy and legislation relevant to the conservation of freshwater SSSIs subject to eutrophication. *Journal of Water and Environmental Management* **10**: 348-354.

Winkler, M. (1981). *Biological Treatment of Wastewater.* Ellis Horword Ltd., Chichester.

Wittgren, H.B. and Maehlum, T.M. (1997). Wastewater treatment wetlands in cold climates. *Water Science and Technology*, **35** (5): 45-55.

Wolstenholme, R. and Bayes, C.D. (1990). An evaluation of nutrient removal by the reed bed treatment system at Valleyfield, Fife, Scotland. In: Cooper, P.F. and Findlater, B.C. (Eds), *Constructed Wetlands in Water Pollution Control,* Pergamon Press, Oxford, pp 139 - 148.

Wood, A (1990). The application of constructed wetlands in South Africa. In: Cooper, P.F. and Findlater, B.C. (eds), *Constructed wetlands in water pollution control,* Pergamon Press, Oxford, pp 235-234.

Wood, A (1995). Constructed wetlands in water pollution control: fundamentals to their understanding. *Water Science and Technology*, **32** (3): 21 - 29.

World Health Organisation (1985). *Appropriate technology for the treatment of wastewaters for small rural communities.* EURO Reports and Studies 90.

Yeoman, S., Stephenson, T., Lester, J.N. and Perry, R. (1988). The removal of phosphorus during wastewater treatment: a review. *Environmental Pollution,* **49**: 183 - 233.

Yin, H. And Shen, W. (1995). Using reed beds for winter operation of wetland treatment system for wastewater. *Water Science and Technology*, **32** (3):111-119.

Zhu, T. and Sikora, F.J. (1995). Ammonium and nitrate removal in vegetated and unvegetated gravel bed microcosm wetlands. *Water Science and Technology*, **32** (3): 219 - 229.

Zhu, T., Jenssen, P.D., Mæhlum, T. And Krogstad, T. (1997). Phosphorus sorption and chemical characteristics of lightweight aggregates (LWA) - potential filter media in treatment wetlands. *Water Science and Technology*, **35** (5): 103 - 108.

Appendix 1

Composition of synthetic sewage

For each 1 l of tap water, the synthetic sewage is composed as follows:

160 mg of bacteriological peptone

110 mg of meat extract

30 mg of urea

7 mg of sodium chloride

4 mg calcium chloride dihydrate

2 mg magnesium sulphate heptahydrate

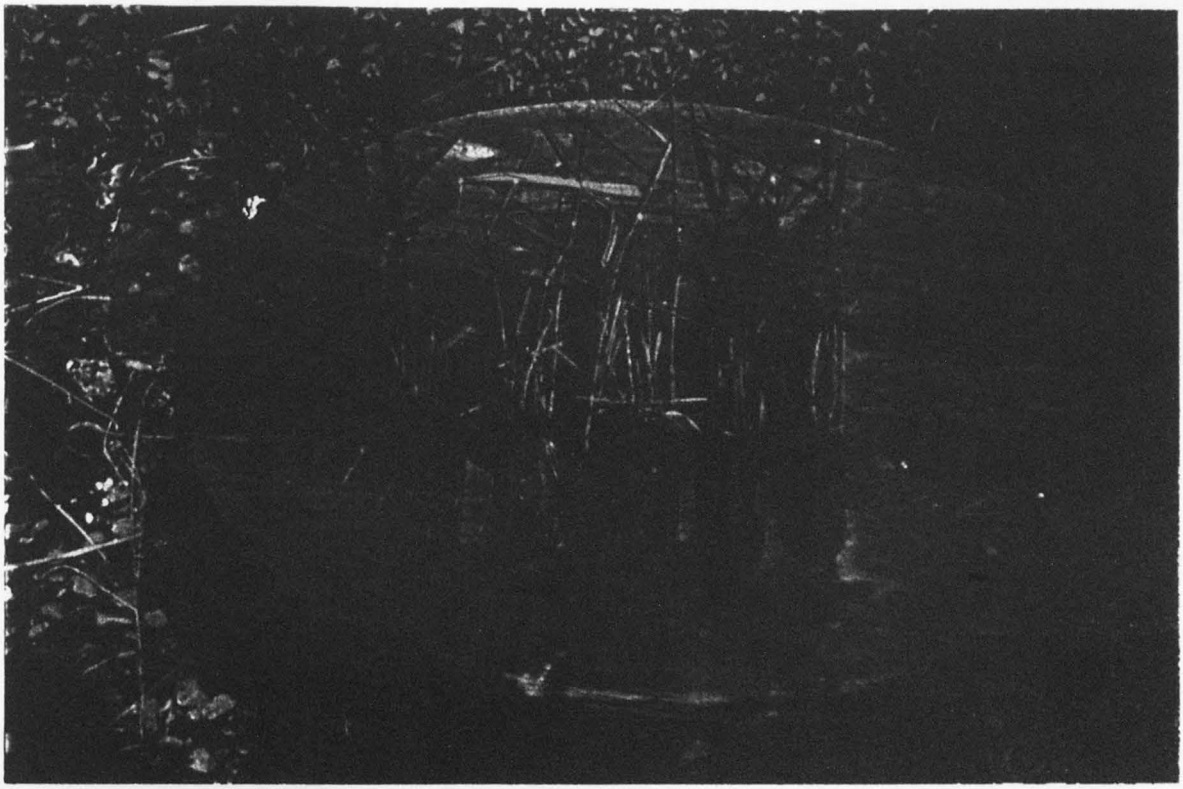
28 mg dipotassium hydrogen phosphate

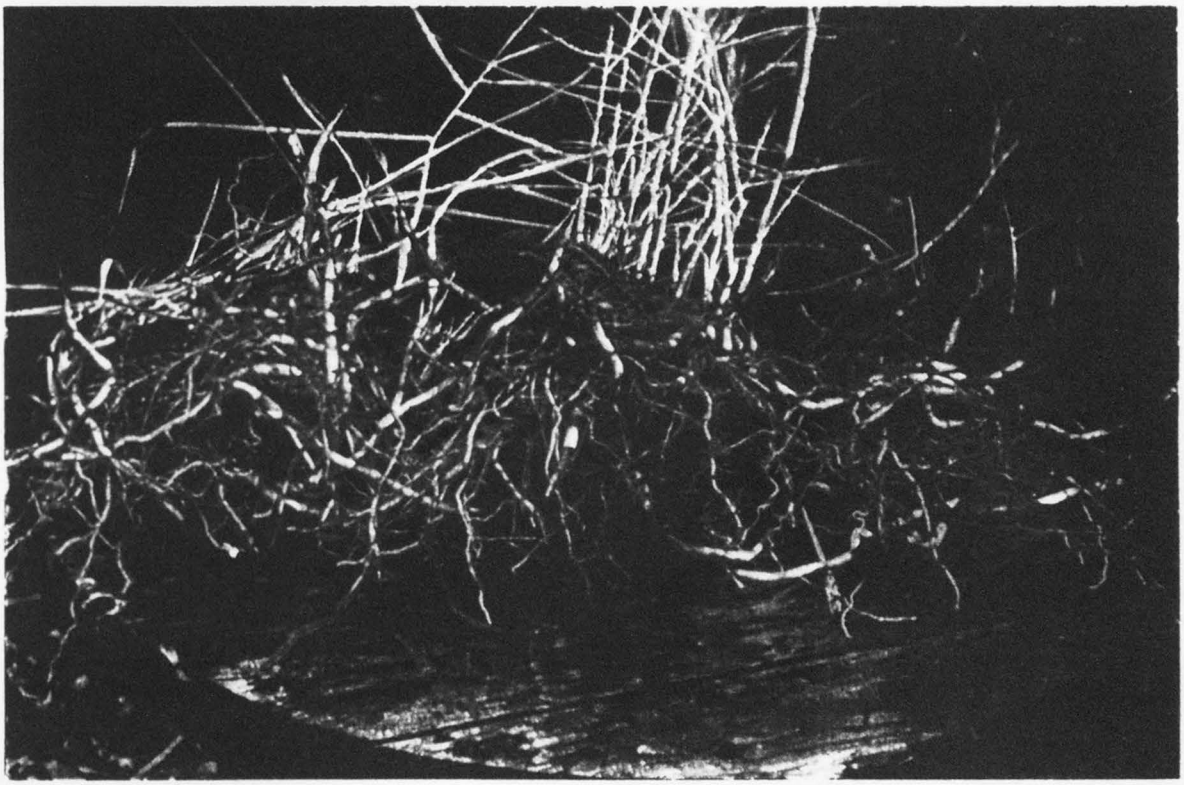
If prepared as a 100 × concentrated solution, it can be stored at 1° C for up to 1 week, and synthetic sewage made daily by appropriate dilution with tap water.

The synthetic sewage after dilution contains approximately 106 mg l^{-1} of organic carbon, 46 mg l^{-1} nitrogen and 5 mg l^{-1} phosphorus (DoE, 1981).

Appendix 2

Phragmites australis rhizomes and root development prior to and after 6 months of growing in a shale substrate.





Determination of bromide concentrations

Bromide concentrations were determined using an ion-selective electrode. 0.5 ml ionic strength adjustor (ISA 1M $NaNO_3$) was added to 25 ml of sample in order to ensure the ionic balance of the samples (Adriano and Doner, 1982). The electrode was inserted into the sample beaker, and the solution stirred continuously for 50 s, then the reading was taken. The electrode response to Br^- concentration was as shown in Figure A3.1. The regression for the response was used to calculate the concentrations in the unknown samples.

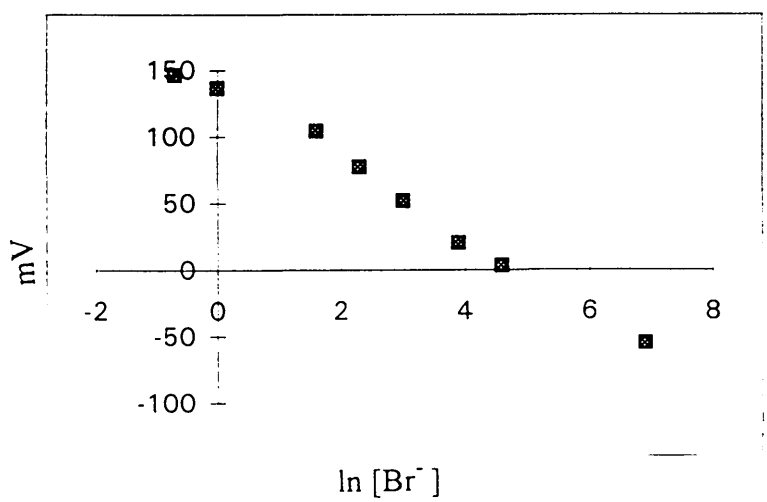


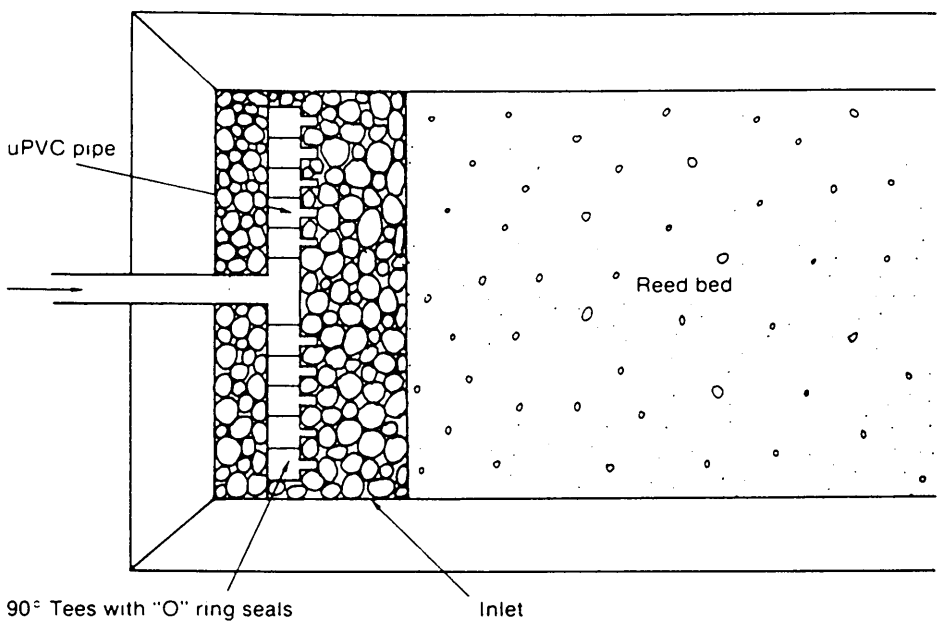
Figure A 3.1: The electrode response to Br^- concentration

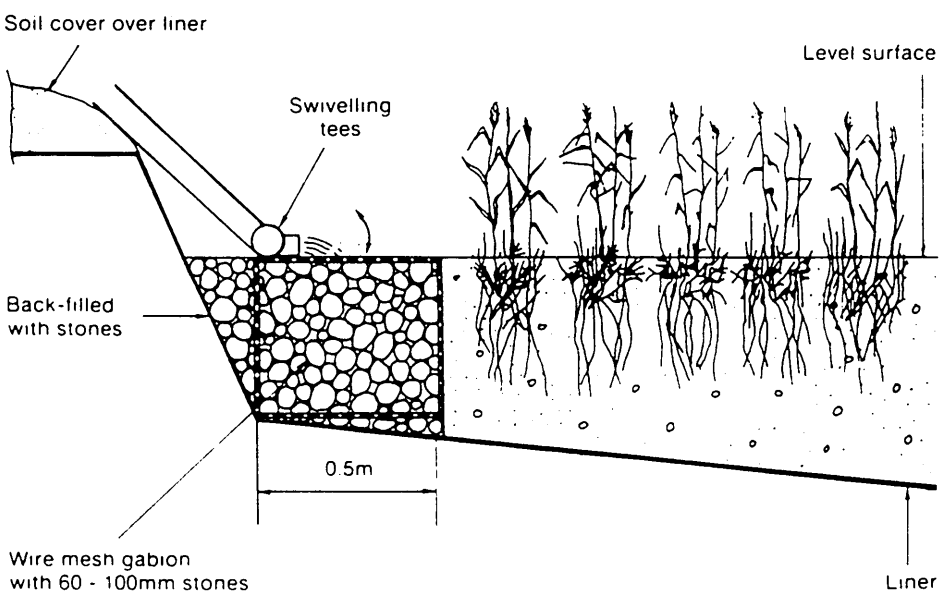
Appendix 4

Detailed plan of Valleyfield reed bed system

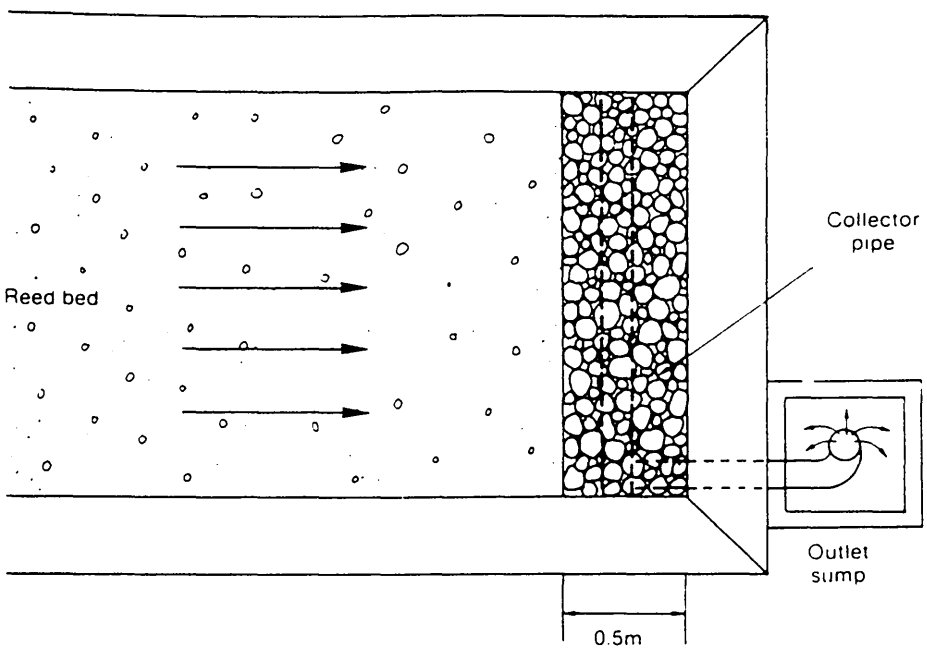
The plan is enclosed in the pocket following this page.

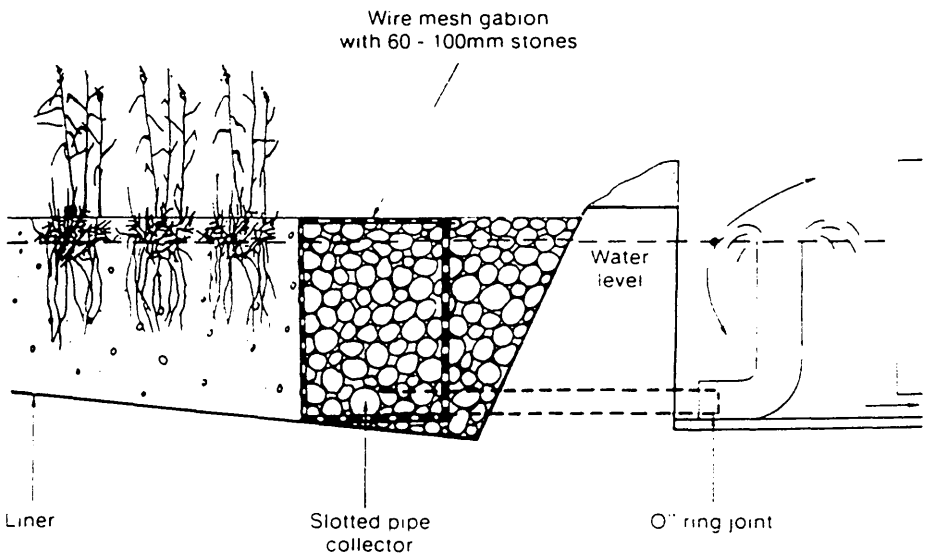
Inlet systems for a CWS





Outlet systems for a CWS





Appendix 7

Phosphate and ammonium removal by constructed wetlands with horizontal subsurface flow, using shale as a substrate

PII: S0273-1223(97)00057-7

PHOSPHATE AND AMMONIUM REMOVAL BY CONSTRUCTED WETLANDS WITH HORIZONTAL SUBSURFACE FLOW, USING SHALE AS A SUBSTRATE

A. Drizo*,**, C. A. Frost**, K. A. Smith* and J. Grace*

* *Institute of Ecology and Resource Management, University of Edinburgh, Edinburgh, UK*
** *Scottish Agricultural College, West Mains Road, Edinburgh EH9 3JG, UK*

ABSTRACT

The objective was to investigate the performance of constructed wetlands with horizontal subsurface flow, using shale as a substrate, in removal of phosphate (P) and ammonium (N) from sewage. Shale was selected on the basis of its physico-chemical properties and its potential for P removal, investigated in an earlier study. A laboratory-scale constructed wetland system (CWS) employing horizontal subsurface flow was set up in a greenhouse, with and without *Phragmites australis* (reeds), and its capacity for simultaneous phosphate and ammonium removal from a synthetic sewage was monitored over a period of ten months. Both the planted and unplanted systems showed an extremely high P removal of 98-100% over the whole period of investigation. Ammonium N was also completely removed in the planted tanks, whereas in the unplanted ones the rates of removal varied between 40 and 75%; removal of nitrate N varied between 85 and 95% in planted and between 45 and 75% in unplanted tanks. pH, E_h and temperature did not differ significantly among planted and unplanted tanks, but the inlet E_h was correlated with P removal ($r^2 = 0.73$; $p < 0.05$). The presence of *Phragmites australis* contributed significantly ($p < 0.05$) to P and N removal. In addition the plants showed excellent growth (up to 2 m in the first year), with good root and rhizome development, and showed potential for heavy metal removal. It was concluded that the shale based system (which uses a readily available material) shows promise as a substrate for constructed wetland systems.

KEYWORDS

Ammonium; constructed wetlands; nitrate; phosphate; *Phragmites australis*; shale; waste water

INTRODUCTION

The capability of wetlands for decontamination of waste water has long been recognised in natural wetlands in many parts of the world (Godfrey *et al.*, 1985; Mitsch and Gosselink, 1993). However, the contrasts in biological and physical characteristics between different wetland types, and difficulties in understanding or predicting the efficiency of such systems, stimulated the development of artificially constructed wetland systems (Hammer, 1989; Cooper and Findlater, 1990; Moshiri, 1993). The major components of such systems which are believed to contribute to waste water decontamination processes are the substrate, the

vegetation (e.g. *Phragmites sp.* (common reed), *Scripus, Typha* (reed mace), *Iris, Glyceria)* and the rhizosphere organisms.

In the case of phosphorus (P) removal, results from several authors (Mitchell, 1978; Richardson, 1985; Swindell and Jackson, 1990) have shown that the immobilisation of P in constructed wetland systems (CWS) occurs through chemical precipitation with metals (Fe, Al, Mn), substrate adsorption of phosphate, bacterial action, plant and algal uptake, and incorporation into organic matter. However, although substrate adsorption is believed to have the greatest influence, the exact contribution of this process to P removal is unclear (Williams *et al.*, 1971; Cooper and Findlater, 1990; Moshiri, 1993). The removal of ammonium (NH_4^+) is largely dependent on the O_2 supply. The bed medium is continuously water-saturated and therefore generally anaerobic. The plants transport oxygen to the rhizosphere, thereby creating aerobic microsites adjacent to the roots and rhizomes in the otherwise reduced substrate. In these microsites, ammonium ions may be oxidised by nitrifying bacteria (*Nitrosomonas*) to nitrite and then (by *Nitrobacter)* to nitrate. Conversely, at a greater distance from the roots, nitrate will be denitrified in the anaerobic region and emitted as gaseous nitrogen to the atmosphere (Brix, 1994; Hammer and Knight, 1994). The present paper describes·

i) simultaneous phosphate (P) and ammonium (N) removal from synthetic sewage in a greenhouse CWS, over a period of 10 months;

ii) the contribution of *Phragmites australis* to P and N removal from waste water, by comparing P and N removal rates in planted and unplanted tanks and calculating the nutrient uptake by the above-ground biomass.

In this experiment, shale was chosen as a substrate for a CWS after a rigorous comparison of the P adsorbing properties of seven different substrates (Drizo *et al.*, 1996).

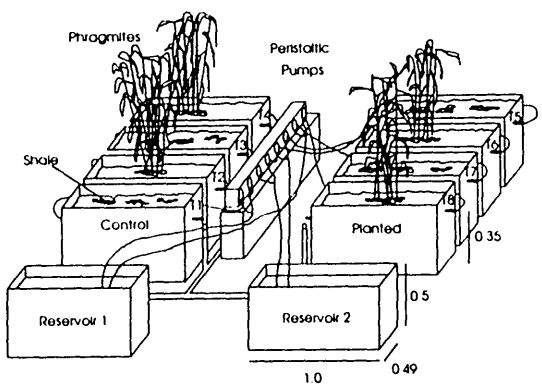


Figure 1. The greenhouse set-up showing arrangement of tanks and reservoirs, and their dimensions (m). Only a few plants are shown.

METHODS

Performance of the greenhouse systems

The CWS was housed within an unheated greenhouse without artificial lighting. Seedlings of ***Phragmites australis*** were grown in a nursery bed of shale until they reached an average height of 0.6 m (4 weeks). Eight 250 l water tanks were each filled with 200 kg of shale. The volume of the material in each tank was 165 l with a pore space of approximately 50 l. Four were planted with seedlings (T2, T8, T4 and T6) and four left unplanted as controls (T1, T7, T3 and T5). They were left to grow for three months before wastewater was applied. Each tank was connected to a reservoir containing 250 l of synthetic sewage, via a peristaltic pump, to circulate the wastewater through the wetland (Figure 1).

The pump was set to operate 4 times each day for 50 minutes, at a rate of 3 l h^{-1}. With this arrangement, 10 l day^{-1} of waste water passed through the system, giving a retention time of 5 days, i.e. the system operated at a hydraulic loading rate of 0.0625 $m^3\ m^{-2}\ d^{-1}$. The surface area of each tank was 0.5 m^2. Real sewage was used only at the beginning of the experimental period, in order to establish a microbial community similar to the real CWS systems. The investigation continued using a synthetic sewage devised by DoE (1981), which was prepared every 5 days. The synthetic sewage (made up by mixing 7 different components: bacteriological peptone, meat extract, urea, sodium chloride, calcium chloride, magnesium sulphate and dipotassium hydrogen phosphate) is widely used as a substitute for the real one in the Water Research Council's waste water treatment studies in Great Britain. Such synthetic sewage after dilution contains approximately 106 mg l^{-1} organic C, 46 mg l^{-1} N and 5 mg l^{-1} P (DoE, 1981). In order to investigate the capacity of the systems for phosphate and ammonium removal over a wider range of nutrient input concentrations, the tanks were fed from two separate reservoirs; four of them (T1, T7, T2 and T8) were fed with average inlet NH_4^+, NO_3^- and $H_2PO_4^-$ concentrations of 8-12 g m^{-3} (0.16-0.24 g $m^{-2}\ day^{-1}$), 0.1-0.2 g m^{-3} (0.002-0.004 g $m^{-2}\ day^{-1}$) and 10-20 g m^{-3} (0.2-0.4 g $m^{-2}\ day^{-1}$), respectively, while the remaining four (T3, T5, T4 and T6) were fed with double these concentrations throughout the whole period of investigation. After 10 months, the inlet phosphate concentration in tanks T3, T5, T4 and T6 was increased to 120 g m^{-3} with the aim to reach saturation. The nutrient concentrations in the synthetic sewage, at the inlets and outlets of the tanks, were monitored every 5 days at the early stages of the experiment, and then once a week. $H_2PO_4^-$ was determined using the standard ammonium molybdate method (DoE, 1980). NH_4^+ was measured using the method by Crooke and Simpson (1971) and NO_3^- by the method described by Best (1976) using a Chemlab Instruments Ltd continuous flow analyser. Additional samples were taken for measurements of pH, redox potential (E_h) and temperature (t) in order to investigate the possible effects of these parameters on P and N removal from waste water. pH and E_h values were measured by standard techniques described by Rowell (1994), using a glass electrode, a reference electrode and a pH meter. Temperature was measured using a combined oxygen electrode and temperature recorder.

Contribution of *Phragmites australis* to phosphate and ammonium removal

The performance of both planted and unplanted tanks in nutrient removal was recorded during the whole period of investigation. In January 1996, the above-ground biomass of the plants was harvested and the fresh weights recorded. Plant material was then oven dried and weighed to determine the dry matter content. Concentrations of mineral elements were then determined using an inductively coupled argon plasma spectrometer (ICP) (DoE, 1986).

RESULTS AND DISCUSSION

Performance of greenhouse tanks

Long term phosphate, ammonium and nitrate loading rates (plan surface area) and corresponding percentage removal rates are presented in Figures 2, 3 and 4, respectively. Virtually complete removal of phosphate (P) was achieved over the whole period of investigation even when the influent concentration rates were increased to 120 g m^{-3} (2.4 g $m^{-2}\ day^{-1}$, Figure 2b) on the last two sampling occasions, for both planted and control tanks. Ammonium was completely removed in the planted tanks, while in the control tanks it varied between 40 and 75%, suggesting that the contribution of the plants was substantial, between 25 and 60% (Figure 3). Nitrate removal at the outlets of planted tanks was between 85 and 95% (with the exception of days 50 and 230) while in unplanted thanks removal varied from 45 to 75% which suggests the contribution of the plants was 20-40%; however, it should be noted that influent nitrate levels were extremely low

(Figure 4). pH, E_h and temperature values are presented on Figure 5. ANOVA was performed in order to test the effects of season and the presence of plants on P and N removal, pH, E_h and temperature (Table 1).

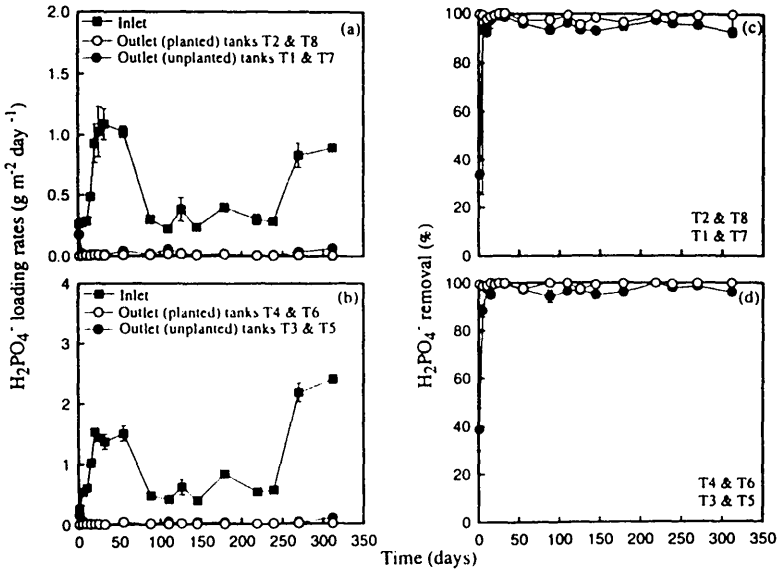


Figure 2. $H_2PO_4^-$ removal for the period from 23/07/1995-20/05/1996. In (c) and (d) open symbols represent removal of phosphate in planted tanks, solid symbols removal in unplanted.
Vertical bars denote standard deviation (sd).

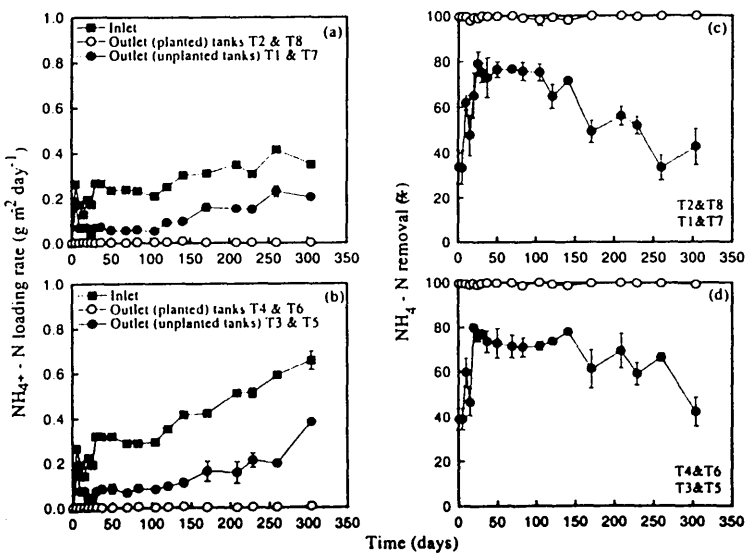


Figure 3. NH_4^+-N removal for the period from 23/07/1995-20/05/1996. In (c) and (d) open symbols represent removal of phosphate in planted tanks, solid symbols removal in unplanted.
Vertical bars denote standard deviation (sd).

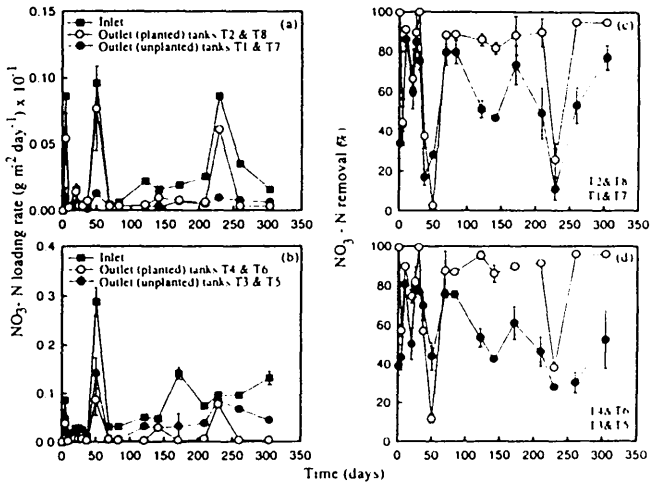


Figure 4. NO_3^--N removal for the period from 23/07/1995-20/05/1996. In (c) and (d) open symbols represent removal of phosphate in planted tanks, solid symbols removal in unplanted.
Vertical bars denote standard deviation (sd).

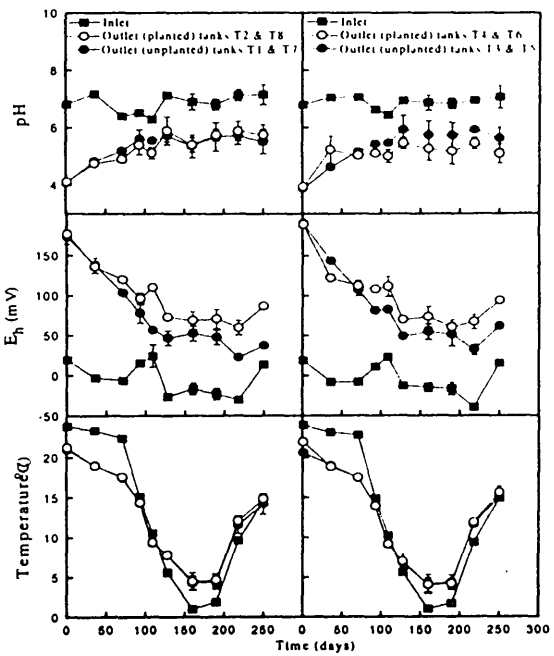


Figure 5. pH, E_h and temperature values for the period from 02/08/1995-06/04/1996.
Vertical bars denote standard deviation (sd).

Contribution of *Phragmites australis* to phosphate and ammonium removal

The presence of *Phragmites australis* in planted tanks contributed significantly to $H_2PO_4^-$, NH_4^+-N and NO_3^--N removal rates (Figures 2-4). However, at lower inlet loading concentrations (T1, T7, T2, T8) for all the investigated parameters, a statistically significant difference between unplanted and planted tanks occurred only for $H_2PO_4^-$ and NH_4^+-N, while for higher inlet loading concentrations (T3, T5, T4, T6) a significant difference ($p < 0.05$) occurred for NO_3-N as well. Seasonal variation had a stronger effect than the presence of plants on the changes in pH, E_h and temperature (Table 1). Plants are believed to have an influence on substrate temperature by acting as an insulation layer and by providing additonal surface area for the development of microbial activity (Wood, 1990). Their effect on the mean influent temperature was not apparent in this study (Table 1).

Table 1. The effects of seasonal variation, presence of *Phragmites* and their mutual interaction on $H_2PO_4^-$, NH_4^+-N, NO_3^--N, pH, E_h and temperature

Parameter	Seasonal variation T_1,T_7,T_2,T_8	Seasonal variation T_3,T_5,T_4,T_6	Planted /unplanted T_1,T_7,T_2,T_8	Planted /unplanted T_3,T_5,T_4,T_6	Interaction T_1,T_7,T_2,T_8	Interaction T_3,T_5,T_4,T_6
H_2PO_4-	$p = 0.19$	$p = 0.72$	$p = 0.004$	$p = 0.004$	$p = 0.2$	$p = 0.65$
NH_4 - N	$p = 0.001$	$p = 0.004$	$p = 0.26\times10^{-7}$	$p = 0.12\times10^{-5}$	$p = 0.001$	$p = 0.004$
NO_3 - N	$p = 0.67$	$p = 0.13$	$p = 0.25$	$p = 0.04$	$p = 0.97$	$p = 0.46$
pH	$p = 0.20\times10^{-4}$	$p = 0.88\times10^{-7}$	$p = 0.83$	$p = 1$	$p = 0.49$	$p = 1$
Eh	$p = 0.70\times10^{-4}$	$p = 0.71\times10^{-4}$	$p = 0.083$	$p = 0.49$	$p = 0.69$	$p = 0.71$
t	$p = 0.49\times10^{-4}$	$p = 0.63\times10^{-5}$	$p = 0.77$	$p = 0.78$	$p = 0.63$	$p = 1$

Elemental analysis of the plants prior to planting, after 3 months growing in shale and after 5 months of the waste water application showed almost no difference in P and N concentrations (Table 2). However, Fe, Mn and Zn concentrations varied considerably ($p < 0.05$) for the three investigated periods: Fe concentration in plants from T2 and T8 decreased by 75% after three months growing in shale and then increased 4.6 times after five months of waste water application (1.1 times if compared with the value prior to planting); in T4 and T6 it followed a similar pattern. Mn concentration in T2 and T8 increased 5 fold after growing in shale for three months, and then by a further 30% after 5 months of waste water application; in T4 and T6 it increased slightly more. Zn concentration decreased by over 70% and then declined still further after a further 5 months. Cu values doubled, then decreased to about the starting concentration but the result was not statistically significant. In addition, an orange, oxidised iron colour was observed on root surfaces. These results indicate the possibilities of *Phragmites australis* for removal of Fe and Mn from waste water. Trace metal absorption by *Phragmites australis* was investigated by Peverly *et al.* (1995), who also demonstrated the precipitation of Fe on the root surfaces. It is possible that such deposits are important for the removal of P from waste water, and future experiments will investigate Fe-P and Mn-P depositions using X-ray fluorescence and scanning electron microscopy techniques.

Table 2. Elemental analysis of plant material harvested prior to planting, after 3 months growing in shale, and after 5 months of synthetic waste water application

Element/DM (concentration)		Prior to planting (March 1995)	After 3 months growing in shale		After 5 months of receiving synthetic waste water application	
			T2&T8	T4&T6	T2&T8	T4&T6
DM*	%	60.3	29.2 (± 0.14)	36.5 (± 5.10)	32.4 (± 3.07)	31.9 (± 4.56)
N	%	1.8	1.9 (± 0.14)	1.5 (± 0.71)	1.5 (± 0.14)	1.6 (± 0.32)
P	%	0.2	0.1 (± 0.02)	0.1 (± 0.05)	0.1 (± 0.06)	0.1 (± 0.01)
Fe	ppm	262.0	65.5 (± 6.15)	69.7 (± 10.87)	300.8 (± 24.80)	345.6 (± 24.00)
Mn	ppm	43.8	221.3(± 14.60)	294.5 (± 47.53)	280.1 (± 23.80)	313.1 (± 39.90)
Cu	ppm	5.7	13.3 (± 2.00)	10.4 (± 3.39)	4.3 (± 0.03)	6.1 (± 1.70)
Zn	ppm	119.0	35.3 (± 0.57)	32.7 (± 4.92)	23.2 (± 5.23)	32.6 (± 3.22)

After the plants were harvested in January 1996, total P and N uptake by above-ground biomass was found to be 2.25 g m^{-2} and 26.2 g m^{-2}, respectively (55 kg P ha^{-1} y^{-1} and 640 kg N ha^{-1} y^{-1}). The value for P is in accordance with the values of 50 to 150 kg P ha^{-1} $year^{-1}$ suggested by Brix (1994), while the value for N is slightly lower (1000 to 2500 kg N ha^{-1} y^{-1}). However, it should be taken into account that most of the nutrients accumulate in the roots and rhizomes (Hiley, 1995) and therefore it is likely that the actual plant uptake was much higher.

CONCLUSIONS

The unplanted constructed wetlands using horizontal subsurface flow showed a very high removal of P (98% throughout the whole period of investigation), with the addition of plants contributing an improvement of just 1% to 99%. After the first year of monitoring the substrate remained equally effective, even when the inlet loading rates were increased 3-fold (from 40 to 120 g m^{-3}, i.e. 0.8-2.4 g P m^{-2} day^{-1}) in order to saturate the four tanks (T3, T5, T4 and T6) receiving the double inlet load. Although shale used in this experiment showed a P adsorption capacity in excess of 0.65-0.7 g P kg^{-1} in an earlier study (Drizo *et al.*, 1996), values as high as 0.8 g P kg^{-1} (unplanted) and 0.825 g P kg^{-1} (planted) were achieved and the tanks were still not saturated which suggests that this material is promising as a substrate for constructed wetlands. Ammonium removal was virtually complete in planted tanks, but in unplanted ones the removal eficiencies varied between 40 and 75%; nitrate removal eficiencies of 85 to 95% in planted tanks and 45 to 75% in unplanted tanks were achieved, although concentrations were low in the inlet water.

There was no statistically significant difference between planted and unplanted tanks in pH, E_h and temperature values. However, there was a correlation between E_h values and P removal.

The presence of *Phragmites australis* contributed significantly to $H_2PO_4^-$ and NH_4^+-N removal rates, but their contribution in NO_3^--N removal was significant only for the higher inlet concentrations (T4 and T6). In addition, plants showed extremely good growth and root development in the shale substrate, achieving a high total surface area for Fe, Mn and P uptake and deposition.

ACKNOWLEDGEMENTS

We thank Mr F Daunt for his great help in the preparation of this manuscript and the construction of the greenhouse systems; Mr R Speirs of SAC for his recommendation on the choice of the substrates at the outset of the research; Mr J. MacGowan of SAC for providing the equipment for P analysis; Mr J. Pearson of Wemyss Brick Co. Fife, Scotland for the supply of shale material; Mr Paul Johnstone for help in establishment of the greenhouse systems and Mr Hannot Elorriaga for artwork.

We acknowledge financial support from the CVCP Overseas Research Scholarship Fund, the Environmental Research Support Scheme (ERSS) of the Soros Foundation (Central European University, Budapest), and the Scottish Office Agriculture and Fisheries Department (SOAFD).

REFERENCES

Best, E. K. (1976). An automated method for determining nitrate - N in soil extracts. *Queensland Agricultural Journal* 33, 161-165.

Brix, H. (1994). Functions of macrophytes in constructed wetlands. *Wat. Sci. Tech.* 29(4), 71-78.

Cooper, P. F. and Findlater, B. C. (eds) (1990). *Constructed Wetlands in Water Pollution Control (Advances in Water Pollution Control. No 11).* Pergamon Press, Oxford.

Crooke, W. M. and Simpson, W. E. (1971). Determination of ammonium in Kjeldahl digests of crops by an automated procedure. *J. Sci. Fd. Agric.* 22, 9-10.

Department of Environment (1980). *Analysis of Raw, Potable and Wastewaters.* HMSO, London.

Department of Environment (1981). *Assessment of Biodegradability. Methods for the Examination of Waters and Associated Materials.* HMSO, London.

Department of Environment (1986). *Methods for the Examination of Waters and Associated Materials.* HMSO, London.

Drizo, A., Frost, A., Smith, K. and Grace, J. (1996). An investigation of possible substrates to enhance phosphate removal from waste water in constructed wetland systems (submitted to *Ecological Engineering*).

Elorriaga, H. (1996). Pilot-scale subsurface constructed wetland performance evaluation on biological oxygen demand (BOD) and suspended solids (SS) removal from synthetic sewage. B.Sc. (Hons.) in Ecological Sciences, The University of Edinburgh.

Godfrey, P. J., Kaynor, E. R., Pelzarski, S. and Benforado, J. (eds) (1985). *Ecological Considerations in Wetland Treatment of Municipal Wastewaters*. Von Nostrand, Reinhold, New York.

Hammer, D. A. and Knight, R. L. (1994). Designing constructed wetlands for nitrogen removal. *Wat. Sci. Tech.* **29**(4), 15-27.

Hammer, D. A. (Ed.) (1989). *Constructed Wetlands for Waste Water Treatment. Municipal, Industrial and Agricultural*. Lewis Publishers, Inc., Chelsea, Michigan.

Henriksen, A. and Selmer-Olsen, A. R. (1970). Automatic methods for determining nitrate and nitrite in water and soil extracts. *Analyst* **95**, 514-518.

Hiley, P. D. (1995). The reality of sewage treatment using wetlands. *Wat. Sci. Tech.* **32**(3), 329-338.

McLean, E. O. (1982). Soil pH and Lime Requirement. In: Methods of Soil analyses, part II, 2nd edition. Chemical and Biological Properties. *Agronomy monograph No 9*. American Society of Agronomy.

Mitchell, D. (1978). The potential for wastewater treatment by aquatic plants in Australia. *Water* (Australia) **5**(3), 15-17.

Mitsch, W. J. and Gosselink, J. G. (1993). *Wetlands*. 2nd edition, Van Nostrand Reinhold, New York.

Moshiri, G. A. (Ed.) (1993). *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers Inc., Baco Raton, Florida.

Peverly, J. H., Surface, J. M. and Wang, T. (1995). Growth and trace metal absorption by *Phragmites australis* in wetlands constructed for landfill leachate treatment. *Ecological Engineering* **5**(1), 21-35.

Rowell, D. V. (1994). *Soil Science: Methods and Applications*. Longman Scientific & Tecnnical, London.

Richardson, C. J. (1985). Mechanisms controling phosphorus retention capacity in freshwater wetlands. *Science* **228**, 1424-1427.

Swindell, C. E. and Jackson, J. A.(1990). Constructed wetlands design and operation to maximize nutrient removal capabilities. In: Cooper, P. F. and Findlater, B. C. (eds). *Constructed Wetlands in Water Pollution Control (Advances in Water Pollution Control. No 11)*. Pergamon Press, Oxford, pp. 107-114

Williams, J. D. H, Syers, J. K., Shulka, S. S. and Harris, R. F. (1971). *Environmental Science and Technology* **5**, 1113.

Wood, A. (1990). Constructed wetlands for wastewater treatment - engineering and design considerations. In: Cooper, P. F. and Findlater, B. C. (eds). *Constructed Wetlands in Water Pollution Control (Advances in Water Pollution Control. No 11)*. Pergamon Press, Oxford, pp. 235-234.